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PHYSICAL REVIEW.

INFRA-RED ABSORPTION SPECTRA:[1] I. GASES.

By W. W. Coblentz.

A SHORT historical review of the literature on this subject is given in a paper[2] presented to the American Physical Society April, 1903. At that time the absorption spectra of about forty organic compounds had been examined far into the infra-red. The results, as a whole, were so complicated that it became evident that in order to gain a better knowledge of infra-red absorption spectra a very extensive and systematic investigation would be necessary. This was made possible by a grant from the Carnegie Institution of Washington, which has been in force since June, 1903.

The total number of compounds now examined amounts to one hundred and thirty-five. Of this number about one hundred liquids and solids, and fourteen gases were explored to 14 μ, using a rock salt prism, while nineteen liquids were explored to 2.5 μ, using a quartz prism. In the meantime a preliminary report has appeared elsewhere[3] which gives a summary of some of the results obtained. The object of the present paper is to give some further results, as well as some details connected with the work.

The apparatus used in this work consisted of a 35 cm. focal length mirror spectrometer, a 7 cm. rock salt prism, and a Nichols radiometer. Except certain improvements, this is fully described else-

[1] Abstract of a monograph on this subject submitted to the Carnegie Institution of Washington for publication.

[2] Phys. Rev., Vol. XVI., p. 385, 1903.

[3] Astrophysical Jour., XX., p. 207, 1904.

where [2] and need not be mentioned here. A considerable portion of the work was repeated to 7.5 μ, using mirrors of 1 m. focal length and 20 cm. aperture, mounted on a large spectrometer.

With this large apparatus the spectrometer slits were 2′ of arc, while in the smaller they were 4′ of arc on the spectrometer circle, so that for the larger apparatus the dispersion was comparable to that of fluorite. With it numerous bands from 6 to 7 μ were resolved, but only occasionally were small bands found in the transparent region, to be noticed later, from 4 to 5 μ, while the region from 3 to 3.5 μ was sometimes found complex.

For the gases a glass cell with rock salt windows on the ends was mounted in vertical ways, between the spectrometer slit and the incident energy, which was supplied by the heater of a Nernst lamp.

For the liquids different kinds of absorption cells were used. Those having boiling-points below 100° C. were placed in rock salt cells, made by bending a fine wire, 0.08 to 0.16 mm. in thickness, into a U-shape, covering it with Le Page's glue, and placing it between two plates of rock salt. After drying, the glue was not attacked by the liquids examined. The top of the cell was covered with tinfoil. The plates of rock salt were split from the natural crystal, about 2 × 3 cm. on an edge, and were more satisfactory than those polished by hand.

Liquids boiling above 100° C. could be used in thinner films, which was an advantage on account of their opacity. For these a ring of tin-foil 0.01 mm. in thickness was placed between the plates of rock salt. Around the outside edge of the plates was placed a strip of pure tin, which was 0.1 mm. thick, and hence easily bent to fit the cell, thus preventing evaporation. This form of cell is much better than that used in previous investigations, in that it can be thoroughly cleaned, while a new tin-foil ring was used for each new compound.

A block of wood having an opening cut in it, over which the rock salt cell was securely mounted, was placed in vertical ways before the spectrometer slit. The radiation from the Nernst heater passed through the opening in the block and through the rock salt cell into the spectrometer slit. A clear plate of rock salt was mounted di-

[2] PHYS. REV., 16, 35, 1903.

rectly below this cell. In this manner no radiation except that which passed through the cell or clear piece of rock salt could enter the spectrometer.

The method of observation consisted in projecting successive portions of the spectrum upon the radiometer vane and noting its deflection when the absorption cell was before the collimator slit, and also the deflection when the clear piece of rock salt was substituted. The ratio of the deflection through the cell to that through the plate of rock salt gave the transmission through the liquid directly, and more accurately than by finding the absorption of the empty cell, and deducting it. This also meant the reduction of the work by almost one-half. After two months' use the difference in absorption of a plate of the absorption-cell and the "clear-plate" was only 3.2 per cent. beyond 3 μ, which is of no significance, since we are not concerned with the question of total absorption.

One of the chief difficulties in this work is to obtain pure chemicals, and it is of the greatest importance to prevent contamination while investigating them. Most of the compounds were imported directly from Kahlbaum, and were the purest obtainable.

Absorption Spectra of Gases.

Our knowledge of the absorption spectra of gases is confined to the work of Ångström[1] who studied CO,CO_2,CH_4,C_2H_4, and $(C_2H_5)_2O$. In fact he is the pioneer in this subject.

In studying gases the chief difficulty lies in obtaining them in a pure state. The apparatus, including generator, purifiers, and gasometers, must be air tight, so that after the air has once been removed, none can enter from outside. Fortunately we have, in liquid air, a means for obtaining small quantities of other gases in a more tangible state. By combining fractional liquefaction and fractional distillation with the usual chemical methods of purification one can obtain gases in a very high state of purity, as will be noticed in the analyses of some of the gases studied. In the present work, the gases were first purified by chemical methods. Several showed absorption bands in common, so the work was repeated,

[1] Ångström, Öfversigt af Kon. Vetensk. Akad. Förhändligar Stockholm, Nr. 7, 1890.

using the additional method of liquefaction. The way that the general transmission has changed and the impurity bands have disappeared as a consequence will be noticed in their transmission curves.

The apparatus for generating and fractionally liquefying the gases consisted of a generating flask, a washing tube, a drying tube containing phosphorus pentoxide, two liquefaction bulbs, and a mercury gasometer (gas-pipette) of 200 cc. capacity. The drying tube was always thoroughly cleaned before making a new gas. The liquefaction bulb was made by enlarging the bottom part of a U-tube which was made from a glass tube bent narrow enough so that it could be inserted into a cylindrical liquid air container.

Petroleum thermometers were used to measure the temperature, which, of course, could be determined only approximately, but as close as one can make the fractional liquefactions. The thermometer was placed in contact with the side of the bulb, and the whole suspended over the liquid air. By raising or lowering this combination any desired temperature could be obtained. The operation consisted in fractionally liquefying the gas in the first bulb, and the part that passed from it into the second bulb was liquefied there at a lower temperature. The part that did not liquefy in the second bulb passed out into the air.

From 5 to 10 c.c. of the liquefied gas were collected in the second bulb, which was then allowed to grow warmer. After the air had been thoroughly washed out, as shown by the lighted gas, the bulb was permitted to become still warmer, and the successive fractions were distilled into the mercury gasometers where they were stored under mercury seals awaiting analysis and examination. This method of procedure, for the present work, was certainly more desirable and efficient than the usual one of joining the generator, purifiers and absorption cell with an exhaust pump. In that case, one cannot manipulate the gases after once generated. The desirability of handling the stored gases is shown in the purification of ethane (Fig. 3), which is almost impossible to obtain in a state sufficiently pure for this work. Not being satisfied with the usual washing in bromine water, and with the liquefaction method, the

gasometer was placed in series with a wash-pipette of fuming sulphuric acid, and the gas was washed back and forth half an hour, after which only a suspicious trace of ethylene remained, as will be noticed at 10.5 μ in the absorption curves, Fig. 2.

The Absorption Cells. — The dimensions of the absorption cells for gases, already briefly mentioned, were: Length, 6.3 and 5.7 cm.; diameter, 2.4 and 2.2 cm.; capacity 30.8 c.c. and 21.5 c.c., respectively.

The rock salt windows were split from the natural crystal which gave smooth, plane surfaces which were not attacked by moisture, and lasted throughout the work of two months. The windows were attached with "Le Page's Glue," which became exceedingly hard on drying, and had such a low vapor pressure that no absorption bands could be detected, even after exhausting the cell to .02 mm. and permitting it to stand four days. One of the vapors to be expected from it would have been acetic acid. Before filling the cell with a new gas, it was always washed out thoroughly with air. This was done by means of a water aspirator attached to the pump, the cell being exhausted from five to seven times, each time allowing it to fill with air. The final exhaustion was carried to .02 mm. and the absorption of the cell, thus exhausted, was found each time before filling it with a new gas. Only once was an absorption found for residual gas; this was ethyl ether, at 8.7 μ, the cell having been washed but three times with air. The gases were introduced into the cells by means of a capillary tube and stop-cock, which was attached to the side of the cell.

A helix of iron wire inserted in the glass cell served as a diaphragm to prevent reflection from the walls, and seemed more serviceable than a black paint, since it also prevented occlusion of gases.

The cell was mounted in the usual manner, in a wooden carrier, which worked in vertical ways, between the source of energy and the spectrometer slit. The transmission through the exhausted cell was found each time before filling with a gas. This also served as a test for residual gas, which could have been detected if present, by setting on one of its absorption bands.

The transmission of the empty cell changed but little in two months, and as a typical example, transmitted 65 per cent. at 1.7 μ

75 per cent. at 4 μ, decreasing to 70 per cent. at 6 μ then gradually increasing to 74 per cent. at 10 μ, and to 78 per cent. at 12 μ. Except regions of selective absorption, the gases, for this length of cell, were usually perfectly transparent, so that such windows were more serviceable and cheaper than highly polished ones, which would have transmitted about 80 per cent. of the energy when new but would have soon become tarnished with moisture.

The slight variation from day to day in the transmission, through the empty cell, was attributed to reflection from the windows. Since two cells were used, on dismounting one, it was not possible to place it in the carrier exactly in the same position each time.

The cell was always securely mounted in the carrier before exhausting and no variation in its transmission could occur while filling it with gas and replacing the whole in the vertical carriers before the spectrometer slit.

Many of the gases, show but few absorption bands for the length of cell used. Whether more exist, which are very weak and can be detected only in layers of great thickness, is an unanswered question. Rubens and Aschkinass[1] using a column of CO_2 gas 65 cm. long found the same number of bands as for one 5 cm. long. On the other hand Langley's curves of the atmospheric absorption, show a great complexity.

METHANE, CH_4.

(Cell 6.3 cm., barom.[2] 750 mm., temp. 22°.)

The methane used in this work was made by heating a mixture of sodium acetate and soda lime, and washing it thoroughly in pipettes of potassium hydrate and of fuming sulphuric acid, which removes the unsaturated hydrocarbons like ethylene. The latter is also formed when methane is made by this method. Since methane boils at — 160° and ethylene at — 105° it is easy to apply the method of fractional liquefaction and fractional distillation. This was done as an additional precaution, but no change in the intensity or position of the transmission maxima, could be detected.

The spectrum of methane, Fig. 1, is distinguished by two large absorption bands at 3.31 and 7.7 μ and a smaller one at 2.35 μ.

[1] Rubens and Aschkinass, Ann. der Phys., 64, p. 584, 1898.

[2] In filling the cell from the gasometer the pressure was made equal the barometric pressure.

Methane was investigated by Angström who found the same number of bands, but since his calibration is wrong beyond 5 μ no comparison can be made.

In discussing that compound it will be noticed that the effect produced be substituting four Cl atoms for the four H atoms of methane

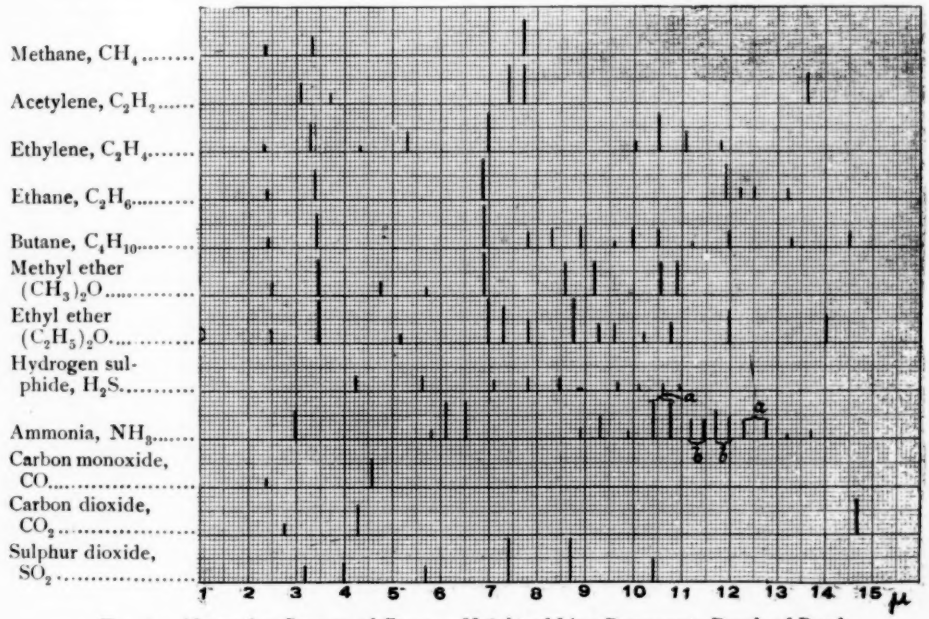

Fig. 1. Absorption Spectra of Gases. Height of Line Represents Depth of Band.

and thus forming carbon tetrachloride, CCl_4, is very striking. There we have an entirely different spectrum, with *no* bands in the region of 3 to 3.5 μ, characteristic to carbohydrates. In fact, carbon tetrachloride has no marked bands except at 6.5 μ and at 13 μ.

Acetylene, C_2H_2.

(Cell 6.3 cm.. barom. 74.5 cm., temp. 22°.5)

The acetylene used was generated from "selected calcium carbide, commercially pure for bicycle lamps."

In the preliminary examination the gas was washed in c.p. H_2SO_4 and dried in P_2O_5. For a subsequent examination the gas was washed by passing it through a solution of 20 gr. of HCl + 10 gr. of $HgCl_2$ + 80 gr. of H_2O to remove the phosphene, PH_3; then through a solution of KOH to remove the H_2S; then through

conc. H_2SO_4 to dry it and finally through a U-tube cooled in CO_2 snow. In the latter there was a slight deposit of vapor on the side where the gas entered. This was found to be water vapor. After all this treatment, as well as an additional one to be mentioned presently, not a single band was changed appreciably in transmission, nor in the position of its transmission minima. That ordinary acetylene is quite pure has been found by Rand,[1] who found a purity of 99 per cent.

Acetylene (see Fig. 1) is distinguished by three deep narrow regions of absorption at 3.08 μ, 7.73 μ and 13.63 μ and two other bands, one at 3.7 which is harmonic with the one at 7.4 μ. In order to be able to locate the band at 13.63 μ the cell had to be exhausted to a pressure of 7 cm. Elsewere the gas is perfectly transparent. At first it seemed that the band at 3.08 μ might be due to water, but washing it thoroughly in new conc. H_2SO_4 and leaving it stand

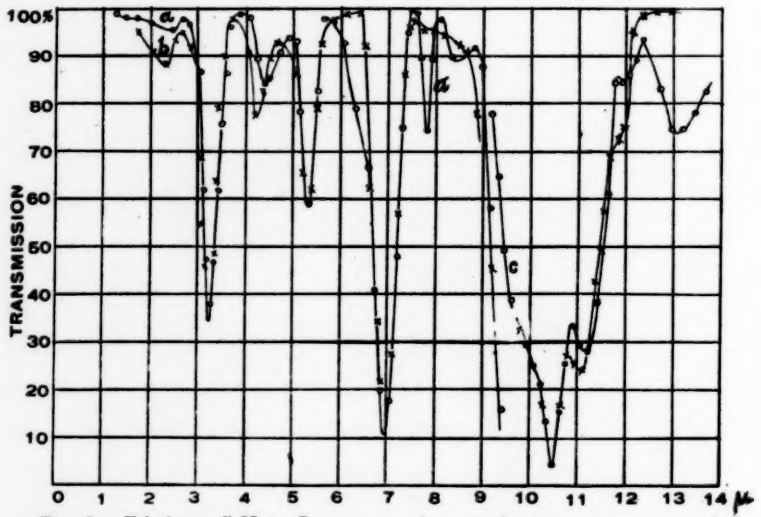

Fig. 2. Ethylene, C_2H_4. Curves: a = impure, b = pure, c = same as b, press. = 20 cm. Hg.

in contact with the acid for three days, in a pipette, failed to alter the intensity or position of this transmission minimum, which would indicate that this band belongs to acetylene.

As a further check, a thin film of water, between fluorite plates, was examined. The first large band was found at 3.01 μ, and the second large band at 6.02 μ.

[1] Rand, PHYS. REV., XIV.

If this band at 3.08 in acetylene were due to water, one would expect a similar one at 6.0, but in this region the gas is perfectly transparent.

ETHYLENE, C_2H_4.

(Cell 5.7 cm., barom. 73.8 cm., temp. 22°.5.)

This gas was prepared from ethylene bromide, $C_2H_4Br_2$ (from Drs. Bender and Hobein, boiling at the theoretical temperature of 131°) by using a zinc-copper couple, and was dried by passing it through a glass tube containing phosphorous pentoxide.

In the preliminary examination the gas showed ether bands. The ethylene bromide was then redistilled and a second examination was made, the gas having been passed through a tube placed in carbon dioxide snow. After the liquid air apparatus was set up, this gas was dried in P_2O_5, then fractionally liquefied in the first bulb, kept at — 97°, and the remainder in the second bulb, kept at — 120°. These were the readings of the petroleum thermometers which, although constant and in contact with the liquefaction bulbs, may not have been at the same temperature since they presented a smaller surface to the evaporating air.

In the first bulb there was a liquid having a strong odor of $C_2H_4Br_2$. In the second tube were about 5 c.c. of liquid ethylene, having a sweet odor much like that of ethylene bromide, but somewhat sharper like pure acetylene. It burned with a beautiful yellowish white flame. The second fractional distillate was used in this examination.

The transmission curves for these three samples of gas, differently prepared, showed but slight variation in the intensity and position of the minima, excepting that the ether band found at 7.8 μ, in the first sample, was absent in the others, Fig 2, curves *a* and *b*.

That the gas was very pure is shown from the analysis, by absorption, using bromine water. The quantity of unabsorbed gas was so small that it could not be measured accurately.

Amount of C_2H_4 taken	50.2 c.c.
Unabsorbed gas	0.6 c.c.
Total C_2H_4	49.6 c.c.
Purity	98.8 per cent.

A combustion analysis, made by Mr. R. C. Snowden, of the first fraction distilled, showed considerable impurity. From general

experience, however, it appears that this is due to the method of analysis rather than to a real impurity.

The transmission of ethylene is entirely different from acetylene, from which it differs in composition, in having two more H-atoms. It is also different from CH_4 in which there is one less C-atom.

The first large band is shifted to 3.28 μ, Fig. 1. The large transmission minima at 6.98 μ and 10.5 μ are of interest in connection with the study of CH_2-groups, and with piperidine.

For the region beyond 9 μ the pressure had to be reduced to 20 cm., curve *c*.

ETHANE, C_2H_6.

(Cell 5.7 cm., barom. 74.5 cm., temp. 23°.)

This was the most difficult gas to be prepared. The chemicals used were more complex than in the case of ethylene and the reaction connot be controlled, so that ethylene, methane, etc., are formed in addition to ethane.

The ethane gas was generated according to the method first described by Frankland[1] who found a "volume purity of 97.88 per

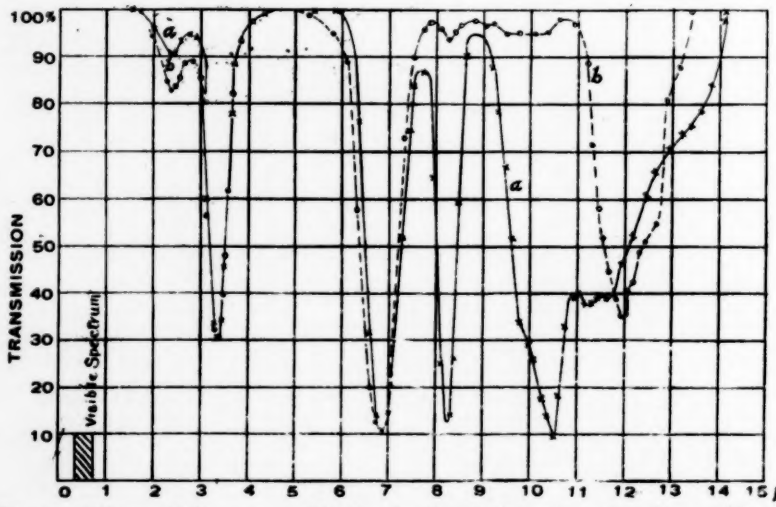

Fig. 3. Ethane, C_2H_6. *a* = purification by liquefaction, *b* = same after washing in fuming sulphuric acid.

cent.," using liquefaction in addition. Equal parts of C_2H_5I (Kahlbaum) and absolute C_2H_5OH were poured over a zinc-copper couple, when the gases began to evolve immediately. No heat was

[1] Frankland, Jour. Chem. Soc., London, 47, p. 236, 1885.

applied since that causes greater impurity. The gas passed through bromine water in a U-tube, with liquid bromine at the bottom, to remove the ethylene, then through KOH to remove the Br, and then through a tube of P_2O_5 to remove the water. Since ethane boils at $-93°$ and ethylene at $-105°$, fractional liquefaction and distillation is an uncertain method of purification. In this case bromine water offers the most serviceable means of separation. Methane will not liquefy till cooled to $-160°$, and hence will pass through the bulb without being condensed. The same is true of the free hydrogen.

After fractional liquefaction (about 6 c.c.) and fractional distillation, the first and second fractions of the distillate were again washed in fuming sulphuric acid and KOH, and dried in P_2O_5, it being thought preferable to run the risk of letting in air in doing so, rather than be uncertain about the presence of ethylene, carbon dioxide, etc.

The analyses were not satisfactory. The second fraction was wasted in two attempts at combustion with oxygen, there being a violent explosion each time. The explosion-pipette method is less accurate on account of the small quantity (5.4 c.c.) of gas that can be used. However, three separate analyses by this method gave a fairly concordant purity of 96 per cent.

This is the first gas noticed in which the absorption bands decrease in intensity or disappear entirely, Fig. 3, which is an excellent clue to the impurities present. The change wrought in the transmission curves is most conspicuous at 10.5 μ. That band, due to ethylene, has entirely disappeared, and the bands at 12 μ, which were obscured by it, now appear in their proper intensities.

The position of the band at 3.39 μ does not vary, however. The very deep band at 8.25 μ which has almost disappeared in the curve *b* is no doubt due to C_2H_5I, used in making the gas, since that substance has a maximum at this point.

Ethane differs from ethylene in having the 2.31 and the 3.28 μ bands of the latter shifted to 2.36 μ and 3.39 μ, respectively. Some of the following gases show this same shifting for the region of 3 μ. As noted before, for rock salt dispersion all carbohydrates studied show a large absorption band, varying in position from 3.1 to 3.5 μ. The same is true for the 1.69 μ band, using quartz dispersion, but

it is difficult to establish a definite shifting as is found for homologous compounds, at from 3.08 μ for acetylene, C_2H_2, to 3.39 μ for ethane, C_2H_6.

This study of gases was undertaken to learn the behavior of the CH_3-group in the molecule, as found in ethane. After studying many compounds of CH_3, simple and complex, having an absorption band at 3.43 μ which was first announced by Julius [1] to be due to CH_3, it was rather surprising to find that ethane, HC_3—CH_3, has its maximum at 3.39 μ.

When we compare ethane, C_2H_6, with benzene, C_6H_6, we find the latter has its transmission minimum at 3.28 μ, which again shows that structure as well as molecular weight influences the absorption.

The cell of ethane was partly exhausted, and 1 part of it was mixed with 2 parts of acetylene, and as a result, the band due to acetylene was obliterated, except a slight break at 3 μ while the band due to both was at 3.3 μ. Lack of time did not permit examination of other regions. The test was not quite a fair one, considering the one gas an impurity in the other, yet it serves to show that, for the region of 3 μ, where the dispersion of rock salt is still small, reliance upon the occurrence of an absorption band of an impurity, as a means for detecting the impurity, is not permissible. However at 4.4 μ where the dispersion is greater, one can detect the presence of CO_2 in CO, see Fig. 4.

BUTANE, C_4H_{10}.

(Cell 5.7 cm., barom. 75.4 cm., temp. 22°.)

This gas was made from ethyl iodide, C_2H_5I, by pouring it over an amalgam made of sodium and mercury.[2] The presence of the murcury retards the action of the metallic sodium upon the ethyl iodide. After drying in P_2O_5 the gas was passed through a U-tube placed in a freezing mixture of common salt and ice.

Butane liquefies at 1° while its isomer liquefies at — 17°. The attempt to liquefy it was not very successful, and the gas collected may have contained the isomer as well as other impurities.

The transmission minima of ethane C_2H_6, at 2.36 μ and 3.39 μ

[1] Julius, Verhandl. Konikl. Akad., Amsterdam, Deel I., No. 1, 1892.

[2] Loury, Jahrsber. in Fortschritte der Chemie, p. 397, 1860.

and 6.85 μ are shifted to 2.4 μ, 3.42 μ and 6.89 μ respectively in butane, Fig. 1. Beyond 7 μ there are a number of bands which occur as impurities. The most conspicuous of these are the two at 7.8 μ and 14 μ found in ether, and the 10.5 μ band of ethylene. The bands at 8.3 and 8.9 μ (diff. = 0.60 μ) find their counterpart in methyl ether, where they are shifted to 8.58 μ and 9.16 μ (diff. = 0.58 μ) respectively, and in ethyl ether where the bands are shifted to 8.75 μ and 9.25 μ (diff. = 0.50 μ) respectively.

Methyl Ether, $(CH_3)_2O$.

(Cell 5.7 cm., barom. 76 cm., temp. 22°.)

Prepared[1] by heating 1.3 parts of alcohol and 2 parts of sulphuric acid to 140°, and washed in KOH to absorb the SO_2 and then dried in P_2O_5.

A study of this gas is of interest in connection with ethyl alcohol, with which it is isomeric. A more striking illustration of the effect of the arrangement of the atom in the molecule upon absorption has not been found, except perhaps in the sulphocyanates and the mustard oils. From 10 to 11 μ alcohol shows transparency and beyond 13 there is complete opacity, while, for methyl ether, the very opposite effect is found. Beyond 8 μ the pressure of the ether had to be reduced to 10 cm.

The only apparent impurity band to be noticed is that of butane at 5.7 μ. The bands at 2.5 μ and 3.45 μ and 10.55 μ are shifted to longer wave-lengths, as compared with those of butane. The 6.9 band is harmonic with the one at 3.45 μ.

This compound like all the gases, is conspicuous for the great depth of its absorption bands.

Ethyl Ether, $(C_2H_5)_2O$.

(Cell 5.7 cm., barom. 74.9 cm., temp. 24°.)

For studying this vapor, some of the anhydrous liquid was placed in the absorption cell, which evaporated, thus giving a saturated vapor. Frequent opening of the stop-cock kept it at about atmospheric pressure.

[1] Erlenmeyer and Kriechbaumer, Berichte d. Deutsch. Chem. Gesellschaft, 7, 699, 1874.

Like methyl ether it has very deep bands, which are shifted as compared with the two preceding gases. The 4.75 μ band of methyl ether occurs at 5.15 μ in ethyl ether. The 6.9 μ band of the former is double in the latter and occurs at 7.0 and 7.3 μ. These two bands are to be noticed in this same region for ethyl alcohol, where there is but one flat band, which would no doubt be found complex, using a larger dispersion.

The 14 μ band is also to be noticed, since it occurs in compounds having CH_3- and C_2H_5-groups, while the 12 μ band is also found in many compounds.

Ethyl ether has been studied by Angström,[1] both as a liquid and as a gas. He found that the maximum at 3.45 μ did not coincide for the two states, the vapor being shifted by 4′ toward the long wave-lengths. He claims to have obtained this effect repeatedly while no shifting was observed by him for other compounds examined in the liquid and the vapor state. In the present work the region of 3.45 μ for liquid ether was explored at the same time that it was for the vapor, but no such shifting was observed.

The bands at 7.3 μ and 7.8 μ almost coincide with those of acetylene. Beyond 7 μ three sets of bands, "Triplets," have "constant differences" of their wave numbers which agree so closely as to lead to the suspicion that they belong to a spectral series.

ILLUMINATING GAS.

The sample used was taken directly from the pipes and examined. It contains bands due to CH_4, C_2H_2, C_4H_{10}, CO, CO_2, SO_2 and H_2S. Ordinary analysis shows about 60 per cent. of CH_4, 6 per cent. of CO, 2 per cent. of CO_2, and the remainder principally unsaturated carbons. The curve is of interest in showing the presence of CO and H_2S.

OXYGEN.

(Cell 5.7 cm., barom. 74.6 mm., temp. 23°.)

Made by heating $KClO_3 + MnO_2$; purified in KOH and dried by passing through a glass tube containing absorbent cotton covered with P_2O_5.

This gas is of considerable interest because it enters into so many compounds. It shows two broad shallow bands at 3.2 μ and 4.7 μ,

[1] Angström, Öfversigt Kongl. Vet. Akad., No. 6, p. 389, 1893.

respectively. They are only 4 per cent. in depth. It appeared that this might be due to impurities, but repeated attempts to remove them failed to change the intensity. After passing the gas back and forth through a tube of P_2O_5, from one gas pipette to another, the bands still existed. The oxygen was then placed for three days in an absorption pipette containing conc. H_2SO_4, but the bands still remained, showing that their presence is not due to water vapor.

One sample was not washed in KOH, and it then showed the Cl band at 4.3 μ. Ångström[1] found this band at 4.28 μ for pure chlorine. It is interesting to note that Dewar and also Olzewski found several absorption bands of liquid oxygen in the visible spectrum.

Hydrogen.

(Generated from c. p. Zn + HCl, washed in H_2SO_4, and dried in P_2O_5.)

This gas showed no absorption bands. Paschen[2] examined hydrogen and nitrogen but, after repeated measurement, failed to find any absorption bands.

Bromine.

The vapor of bromine showed no bands. To prevent it from attacking the glue, the cell was lined with paraffine.

Carbon Monoxide, CO.

(Cell 5.7 cm., bar. 73.2 cm., temp. 23°.)

Made by heating oxalic acid, $C_2H_4O_2$ and conc. H_2SO_4. This forms CO, CO_2 and H_2O. The CO_2 was absorbed by passing the gas through KOH solution after which the CO was dried in P_2O_5.

As will be noticed in curve *a*, Fig. 4, there was still some CO_2 present as shown by the maxima at 2.75 μ and 4.3 μ. After washing the gas back and forth, for half an hour, in a burette of KOH,

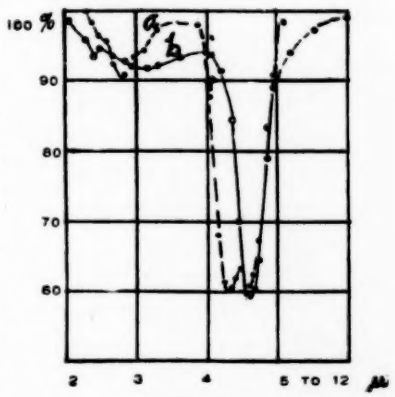

Fig. 4.

$a = CO + CO_2$. $b = CO$

[1] Ångström and Palmer, Öfversigt Kongl. Vet. Akad., No. 6, p. 389, 1893.

[2] Paschen, Ann. der Phys., Vol. 53, p. 334, 1894.

and drying in P_2O_5, the CO_2 was entirely removed as shown by curve *b*.

The maxima of CO occur at 2.4 μ and 4.6 μ. Ångström [1] found these maxima at 2.48 and 4.52 μ.

The absorption spectrum of CO was examined at 14 μ, but no maxima were found.

As shown by Ångström, the fact that the CO band occurs at 4.6 μ and the CO_2 at 4.3 μ invalidates the assumption that molecular weight has a great influence on absorption.

CARBON DIOXIDE, CO_2.

(Cell 5.7 cm., bar. 74.0 cm., temp. 23°.)

Made from $K_2CO_3 + H_2SO_4$ and dried in P_2O_5.

This gas has been examined by nearly every person who has investigated absorption spectra. It is noted for its variation in the location of its maxima in emission and absorption spectra. This is most evident at 4 μ and 14 μ.

The emission [2] band of a bunsen burner occurs at 4.4 μ, while the atmospheric absorption band occurs at 4.28 μ. Rubens and Aschkinass,[3] using a sylvite prism, studied CO_2 to 20 μ and found a large band at 14.7 μ for absorption and at 14.1 μ for emission. The column of CO_2 in the absorption work was 65 cm. in length. It will thus be noticed that at 4.28 μ the emission band shifts to the longer wave-lengths with rise of temperature, while at 14 μ the shift is towards the shorter wave-lengths.

Angström found the CO_2 bands at 2.6 μ and 4.32 μ, while in the present examination they occur at 2.75 μ and 4.29 μ. The fact that the atmospheric band of CO_2 occurs at 4.26 μ leads me to think that the present value is more nearly correct. A slight trace of CO would tend to shift it toward the band at 4.58 μ. The 14.66 μ band is in excellent agreement with the value, 14.7 μ, found by Rubens and Aschkinass,[2] when we consider that rock salt is already quite opaque in this region. As a whole, the work agrees well with that of other observers, considering how precarious a problem it is to map infra-red absorption spectra.

[1] Ångström, loc. cit.

[2] Paschen, loc. cit., Vol. 53.

[3] Rubens and Aschkinass, loc. cit.

Carbon dioxide is the only gas studied that has *no* absorption bands between 4.5 μ and 14 μ, Fig. 1.

From the fact that gases dissociate at high temperatures, are we to conclude that as the temperature rises the CO_2 dissociates into CO, thus shifting the maximum of CO_2 at 4.26 μ toward that of CO at 4.6 μ?

Sulphur Dioxide, SO_2.

(Cell 6.3 cm., bar. 74.4 cm., temp. 23°.)

Generated by adding conc. H_2SO_4 to sodium bisulphate, $NaHSO_3$, and drying in P_2O_5.

This same gas was fractionally liquefied and then fractionally distilled, but the curves coincided for the two samples, showing that nothing has been eliminated. This is a striking contrast to ethane, in which for successive purifications certain bands continued decreasing in intensity, showing that they were due to impurities.

Compared with CO_2 we have few examples which are more conspicuous in showing marked changes by substituting an S- for a C-atom.

In the region where CO_2 is transparent the SO_2 has its greatest absorption bands. The one at 10.4 μ coincides with that of ammonia.

Hydrogen Sulphide, H_2S.

(Cell 5.7 cm., bar. 74.0 cm., temp. 21°.)

Generated by adding HCl to ZnS, dried in P_2O_5.

Liquefied in two fractions, one at $-15°$ the other at $-60°$. The sample liquefied at $-60°$ was distilled fractionally and several fractions examined. A sample which had been made from ZnS + H_2SO_4 but not liquefied, showed SO_2 bands which would naturally be expected.

The changes wrought in the absorption spectrum by substituting hydrogen for oxygen are not so marked as that from CO_2 to SO_2. For H_2S, we have a greater number of lines, especially beyond 9 μ, but there are no deep bands as in SO_2. It was noticed that the bands were not so intense after the gas had stood awhile. Whether this is due to decomposition has not been determined, on account of lack of time. Certain samples tarnished the mercury, while others did not after standing in the gasometer for some time.

AMMONIA, NH_3.

(Cell 6.3 cm., bar. 74.8 cm., temp. 22°.5.)

Made by heating NH_4Cl and solid KOH, and drying over freshly heated CaO. Upon finding several bands in common with those of certain carbohydrates, and that NH_2CH_3 or $NH_2C_2H_5$ might be present in the NH_4Cl, the latter was purified according to the method of Stas[1] by boiling with HNO_3 for half a day. The gas was liquefied in order to remove the supposed water band at 2.95 μ. A sample was placed in a combustion pipette, containing freshly-heated CaO over mercury, for five days, when the band at 2.95 μ was found to be as intense as on previous determinations. Moreover, the absorption band of water was found at the same time, at 3.0 μ, which shows that the 2.95 μ band is a characteristic band of ammonia.

It will be noticed elsewhere that this band is to be found in compounds containing amido-, NH_2, groups, as well as in certain ones containing nitrogen.

Ammonia is one of the most interesting compounds studied, because of the numerous deep narrow bands from 9 μ to 13 μ. At 5.7 μ and 7.3 μ there is evidence of existing bands, but the narrow dispersion of rock salt prevents their being resolved. This is the only compound studied having such a series of maxima, which are, in addition, so regularly distributed that it reminds one of the ammonia and the hydrogen spectrum in the optical region. Whether the "law of constant difference" of the wave numbers is true, or whether the coincidence in the values of certain wave numbers is simply accidental, is difficult to decide with the few examples at hand. We have the following examples:

I.	II.	III.
$\frac{6.1\mu}{6.5} > V_0 = 100$	$\frac{10.4}{10.75} > V_0 = 31$	$\frac{11.18}{11.43} > V_0 = 20$
$\frac{9}{10} > V_0 = 112$	$\frac{12.30}{12.78} > V_0 = 31$	$\frac{11.69}{11.98} > V_0 = 22$

It thus appears that there are three subordinate series, but how are we to establish the validity of these observations? More pairs

[1] Stas, Fresenius Zeit. f. Anal. Chemie, 6, p. 423.

of bands are necessary, but, as we approach the visible spectrum, the pairs of maxima must lie closer together, and hence can only be resolved with a larger dispersion. In addition to this, the regions at 2 μ and 4 μ are quite transparent. This however can probably be remedied by using longer columns of the gas.

THE ELIMINATION OF GAS ACTION IN EXPERIMENTS ON LIGHT PRESSURE.

BY G. F. HULL.

THAT a beam of light falling on a vane suspended in a partial vacuum produces pressure has been established experimentally by Lebedew and by Nichols and Hull.

The accurate measurement of the pressure of a beam of definite energy has been made by Nichols and Hull and its value has been found to agree very closely with the value as determined theoretically by Maxwell and by Bartoli. But in each case these experiments were carried on for three or four years and required for their successful termination a fairly complete knowledge of the action which takes place among the gas molecules of a partial vacuum when a beam of radiation falls upon a suspended vane. It was with the object of making the phenomenon one easier of repetition that the following experiments described in this paper were undertaken.

The essential point in demonstrating the pressure due to radiation is the elimination of the "gas action" on the vane. Lebedew attempted to do this by using very thin vanes and high vacua. The exact value of this vacuum is not stated by Lebedew, but judging by the precautions taken it must have been of the order of 0.00001 mm. Even with this difficulty maintained vacuum the deflection of his torsion system differed from that due to light pressure by amounts as great as 80 per cent. of the latter.

The arrangement of apparatus and the methods used by Nichols and Hull were as follows:

1. The vane was silvered. Thus the radiation pressure was twice as great and the gas action about one tenth as great as the corresponding effects had a black surface been used.

2. The pressure of the air in the receiver was varied until the gas action was a minimum.

3. Throws were taken with the silvered side of the vane towards and away from the light; the argument being that the gas action

upon the warmer (the silvered) side of the vane would thus be in opposite direction in the two cases while the light pressure would be unchanged in sign.

4. Exposures of one quarter of the period of the torsion system were made.

The results show that using silvered surfaces and taking a large number of observations into account the mean deflection did not differ from that due to light pressure by more than 1 per cent. of the latter. The analysis of any one set of observations, however, shows that gas action was, in general, present, that it might differ in sign on the two vanes, and that in certain cases it did not reverse when the torsion system was reversed. This curious behavior of the gas action could not be accounted for upon any hypothesis which the authors were then able to formulate.

The preliminary experiment in the present series was one to test the nature of the gas action when the air pressure in the receiver was varied from about half an atmosphere up to a few millimeters of mercury. For this purpose a rectangle of glass 14 × 10 × 0.1 mm. was fastened by shellac to a fine glass rod which formed the rotation axis of the torsion system. To this rod, at right angles to the plane of the vane, was attached a fine aluminum wire upon which a small counterpoise weight could be placed. By means of this weight the vane could be made strictly vertical or it could be inclined to the vertical. At first the vane was inclined a few degrees to the vertical. It was blackened on one side sometimes by a spray of lampblack in ether, sometimes by camphor smoke. The radiation from a Nernst lamp, whose variations in intensity were corrected by a wattmeter, was allowed to fall upon one half of the vane and the turning points were read by a telescope and scale. The mean curve for both halves and both positions of the surfaces was then plotted from which the nature of the gas action was evident. This was done for air pressures from half an atmosphere up to 1 mm. of mercury. Then the suspension was taken down and without changing the angle of inclination the blackened side was cleaned and the cleaned side blackened. It was now found that for air pressures from half an atmosphere to 10 mm. the gas action, when the black side was away from the light, was the same as it

was in the previous case with the black side towards the light, and *vice versa*. Reversing the suspension of course altered the inclination of the vane from $+\theta$ to $-\theta$; the gas action was also reversed, not because the absorbing surface had changed position, but because the inclination had changed sign. It is evident that this action, depending chiefly upon the inclination of the vane and not upon the position of the warmer face, is due to convection. It thus may happen that, in the case of vanes suspended from hooks, the gas action on one vane may differ in sign from that on the other; moreover, that this action may not be reversed when the system is turned through 180°.

By varying the degree of vacuum, the nature of the black surface and the inclination of the vane, it was also shown that there are at least two kinds of gas action which depend upon the surface heated and not upon the inclination of the vane, and which are more effective at high vacua. One, which may be called the rocket action, depends upon the nature of the surface, *e. g.*, the thickness of the black coating, and is due to the projection from the warmer surface of gas particles absorbed by it. The other action is the true radiometric effect — the bombardment of the vane by the more active gas molecules. A more complete study of these various actions is now being carried on in this laboratory.

In order that the convection action may be eliminated it is necessary that the vane be made strictly vertical. This was done by the ordinary optical methods used in adjusting a spectrometer. To test the value of this adjustment a vane silvered on one side was made vertical. The radiation was allowed to fall on the vane for half its period — about five seconds — then it was cut off and the return throw was read. The difference between the mean of the zeros and the first turning point gave the *throw*. This throw was taken both right and left of the axis, then the suspension was turned through 180° and the corresponding throws were found. The mean of the throws was determined for various air pressures and the constancy of the result is shown by the fact that from 160 mm. to 5 mm. the throws did not differ by more than 1 per cent. from the average of this interval.

The convection or windmill action may be eliminated by making

the vane vertical. The other two effects may be eliminated by bottling them up — by enclosing the absorbing or reflecting surfaces in a non-absorbing envelope which moves with it. The ideal arrangement would be a very light cylindrical capsule with thin glass or flourite ends and having the absorbing or reflecting surface midway between the ends, the whole suspended from one arm of a torsion balance. One side of this inner surface might be blackened, the other side silvered so that the torsion system under the action of light pressure would rotate in exactly the opposite direction to that of a Crookes Radiometer. The arrangement (discussed in our earlier work but rejected for exposed silver surfaces), here adopted was that shown in horizontal section in fig. 1. The silvered side of the cover glass and the blackened surface of another glass of equal thickness were placed in contact. The glasses were attached to each other by traces of wax at the corners. To the outer surfaces of these glasses, but separated from them by small glass rods, were attached two other glasses. The arrangements on both sides of the rotation axis were similar. When the blackened surface is exposed to the light source the radiation, decreased in intensity by the slight reflections at the glass surfaces, falls upon the black surface and is there absorbed. Owing to the equal amounts of gas and air space between this surface and the outer surfaces the latter should experience equal increases in temperature. Hence the radiometric action on the two faces should be equal — the whole system being in the axis of a cylindrical jar. If the surfaces are vertical the convection action should be negligible. Hence the throw when the radiation falls upon the black surface should be to that when it falls upon the silvered surface as the light pressures on the two surfaces ; *i. e.*, as the energies per unit volume in front of these surfaces.

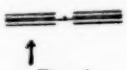

Fig. 1.

The reflection coefficient for this kind of radiation from air-glass and glass silver surfaces has been found to be 78 per cent. Assuming that the reflection coefficient from air-glass is 4 per cent. and from glass lamp-black is 1 per cent., the total reflected energy on the black side is approximately 13 per cent. Hence the throw when the light falls upon the silvered surface ought to bear to that obtained when it falls on the black surface the relation of 1.78 to

1.13 or 1.58 nearly. The table shows that for the range of air pressure from 30 to 70 mm. of mercury the experimental value of the ratio differs from the theoretical value at most by 2 per cent.

TABLE I.

Pressure of Air in mm.	Silver Exposed.	Black Exposed.	Ratio.
10	320	350	0.92
20	280	190	1.47
30	261	166	1.57
40	256	162	1.58
50	251	158	1.59
60	251	157	1.60
70	250	155	1.61
100	250	170	1.47
150	253	198	1.28
200	255	267	0.95

The data shows that on a protected black surface the gas action may be eliminated to within 1 per cent. of the radiation pressure. Therefore the gas action present when radiation falls on a protected silver surface would be eliminated under the same conditions to within one twentieth of 1 per cent. But it would be difficult to measure the energy of the light source to this amount, so that further refinements in the elimination of gas action are unnecessary.

Without changing the arrangement in any other way the outer surface on the black side was blackened. The throws obtained by radiation falling upon this exposed surface were compared with those falling upon the protected silver. The best value of this ratio in the most favorable region of air pressure was 0.75 in place of 1.75.

At the Cambridge meeting of the British Association for the Advancement of Science, Professor J. H. Poynting described an arrangement used by him in which the vane upon which the radiation fell was normal to the cross arm which in turn was attached at right angles to the rotation axis. If the surface of the vane is blackened the torque due to radiation pressure is equal to the energy of the beam per cm. of its length multiplied by the mean distance from the axis to the line of central intensity of the beam. If all the radiation falls on the black vane it is unnecessary to consider the angle of incidence or the shape of the vane. The forces due to gas

action theoretically should be at right angles to the surface and therefore parallel to, if not coincident with, the cross arm. Their moment may therefore be made zero. A torsion system similar to, but only one third the size of, Professor Poynting's arrangement was set up and throws were taken for various air pressures. A number of surfaces were used, thick and thin coatings of camphor black, lampblack deposited by spray and silver black. The surfaces were sometimes *exposed*, sometimes covered, *i. e.*, two glasses were used with the coating between them. All of these, for almost all air pressures from 0.1 mm. to atmospheric pressure, proved, to the surprise of the writer, very unsatisfactory. Only in a limited region of air pressures from 40 to 60 mm. of mercury were the throws at all constant, and even in this region considerable differences in the throws could be obtained by slightly altering the position of the light spot on the vane. These differences were not due to changes in the moment arm, but were due to differences in gas action. This result may be accounted for upon various hypotheses : (1) The gas action is not necessarily normal to the surface when light is incident obliquely, but depends on the surface. (2) The gas action produces a torque when it is not coincident with the cross arm. (3) Gas action at an edge may produce a torque when the light spot is nearer one edge than the other. The last two effects may be eliminated by making the vane cylindrical in shape and wide compared with the light beam. After some experience it was not difficult to make cylindrical sectors of glass of pretty accurate curvature by moulding cover glasses, 0.1 mm. in thickness, between brass cylindrical surfaces which had been carefully turned and worked into one another. A sector of 1 cm. radius and 1.5 cm. arc was mounted by small glass rods so that the rotation axis was at its center of curvature (Fig. 2). The sector was silvered on its inner surface so that this adjustment could be made optically to a close degree of accuracy. It was counterpoised so that the axis was vertical. If the gas action is normal to the surface then its moment about the axis should equal zero for all positions of the light spot on the vane.

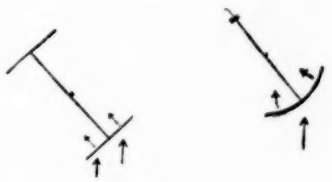

Fig. 2.

It was found that this was very far from being true for all the different kinds of black surfaces used. The silver black gave the best results, though in this case a good deal of the radiation was reflected and consequently the torque due to radiation pressure was small.

A thin vane of clean clear glass, accurately vertical and mounted radially may be used to advantage to demonstrate light pressure. If the light has been filtered through a considerable thickness of glass there will be but little absorption by the thin vane and its two surfaces will be warmed nearly equally. Consequently the radiometric effect will be small. The reflection of the radiation of the two surfaces will make a difference of about 16 per cent. between the energy in front of and behind the vane. Hence the light pressure will be about one sixth of that due to the same light beam falling upon a black surface. The throws for such a vane had only about a ten per cent. variation in a range of air pressures from about 10 mm. to 200 mm. of mercury.

Another arrangement of surfaces (Fig. 3), though not so satisfactory as the enclosed surfaces earlier described, was used. Two brightly silvered glass rectangles were fastened obliquely to cross arms in such a way that they were parallel to one another and to the rotation axis and had their silvered surfaces, one towards, and the other away from, the axis. Light was so incident on one as to be reflected along the cross arm and then in a direction parallel to its original direction. The incident and emergent beams produced pressure torques in the same direction, but the effects due to gas action, if the vanes were both vertical, were opposite in direction, though not equal in amount, owing to the differences in the reflection coefficients of air-silver and glass-silver surfaces. Oblique incidence increases the reflection coefficients and decreased absorption. Moreover, by using polarized light, with the electric vibration parallel to the surface, these absorption coefficients were again decreased.

Fig. 3.

Readings were taken for light, natural and polarized in and perpendicular to the plane of incidence. The data shows that in the case of light polarized in the plane of incidence the readings were fairly constant for air pressures from 20 to 100 cm. of mercury.

When the plane of polarization was turned through a right angle the gas action became more than four times that in the previous case. The gas action for natural light was midway between the two.

The various methods here described show that a more complete elimination of the gas action, than has been obtained heretofore, results from enclosing the absorbing or reflecting surface and making the surfaces vertical. The obvious characteristic of light pressure in contrast to gas action, viz., the greater pressure on the reflecting surface, may easily be shown by this arrangement.

The writer is indebted to Professor N. E. Gilbert for continuous assistance in these experiments.

WILDER PHYSICAL LABORATORY, DARTMOUTH COLLEGE,
HANOVER, N. H., December, 1904.

THE TORQUE BETWEEN THE TWO COILS OF AN ABSOLUTE ELECTRODYNAMOMETER.[1]

BY GEORGE W. PATTERSON.

AN absolute electrodynamometer employing two single layer coils, similar to an instrument described by the writer and Dr. Karl E. Guthe in a paper read before Section B of the American Association for the Advancement of Science, is at present being used by Professor Henry S. Carhart and the writer in an absolute determination of the electromotive force of standard cells. The former instrument was employed by Patterson and Guthe[2] in a determination of the electrochemical equivalent of silver, and by Carhart and Guthe[3] in a determination of the electromotive force of the Clark cell. Both instruments were designed to take advantage of a simple formula given by Gray[4] for the case in which the centers of the axes of both coils are coincident and both coils have lengths $\sqrt{3}$ times their radii respectively.

The following derivation of a general formula is along different lines from that of Gray, but leads to the same conclusion. I have thought it desirable to consider the effect which the asymmetry of the leading wires might produce and also the effect of the earth's magnetic field, with a view to the elimination of these effects from the final result.

It will be assumed in advance that the magnetic field at points near the axis of a single layer coil of fine wire carrying a current is equivalent to that produced by a current sheet of the same effective radius and of the same number of ampere turns; and that the torque produced on the suspended coil, wound with a copper rib-

[1] Read at the Washington meeting of the American Physical Society, April 22, 1904.

[2] Patterson and Guthe, Proc. A. A. A. S., 1898, p. 154, and PHYSICAL REVIEW, Dec., 1898, Vol. VII., p. 257.

[3] Carhart and Guthe, Proc. A. A. A. S., 1899, p. 103, and PHYSICAL REVIEW, Nov.–Dec., 1899, Vol. IX., p. 288.

[4] A. Gray, Theory and Pract. Absolute Meas. in Elect. and Mag., Vol. II., part I., p. 275.

bon, is equal to that which would be obtained with a corresponding current sheet as suspended coil.

First let us find the strength of the magnetic field at a point P (Fig. 1) on the axis OP of a circular turn of wire carrying a current of intensity I. The point P is at a distance r from the wire, and ξ from the center O of the circle which has a radius R. The strength f of the magnetic field at the point P is

$$f = \frac{2\pi R^2 I}{(R^2 + \xi^2)^{\frac{3}{2}}}. \tag{1}$$

The magnetic potential V_s at the point P is

$$V_s = -\int_0^{\xi} f d\xi = -\frac{2\pi I \xi}{\sqrt{R^2 + \xi^2}}, \tag{2}$$

The potential at the point O is taken as zero.

The potential V_0 at P (Fig. 2) due to the same current I passing

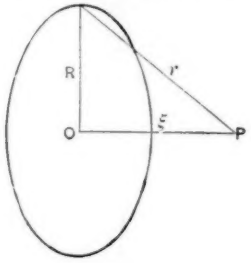

Fig. 1.

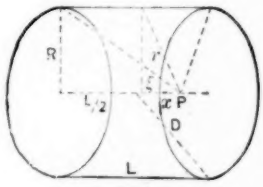

Fig. 2.

through n turns of fine wire wound on a cylinder of length L, with an effective radius R, is

$$V_0 = \frac{n}{L}\int_{x-\frac{L}{2}}^{x+\frac{L}{2}} V_s d\xi = -\frac{2\pi n I}{L}\left[\sqrt{R^2 + \left(x + \frac{L}{2}\right)^2} - \sqrt{R^2 + \left(x - \frac{L}{2}\right)^2}\right].$$

As the right hand term of this equation does not develop into a series which is convenient, we shall introduce the value of the half diagonal D obtained from the relation

$$D^2 = R^2 + \frac{L^2}{4}.$$

We obtain:

$$V_0 = -\frac{2\pi n I D}{L}\left(\sqrt{1 + \frac{x(x+L)}{D^2}} - \sqrt{1 + \frac{x(x-L)}{D^2}}\right). \tag{3}$$

When (3) is expanded and the collected terms arranged by powers of x, we obtain

$$V_0 = -\pi nI\left[2\frac{x}{D} - \left(1 - \frac{1}{4}\frac{L^2}{D^2}\right)\frac{x^3}{D^3} + \left(\frac{3}{4} - \frac{5}{8}\frac{L^2}{D^2} + \frac{7}{64}\frac{L^4}{D^4}\right)\frac{x^5}{D^5}\right.$$
$$- \left(\frac{5}{8} - \frac{35}{32}\frac{L^2}{D^2} + \frac{63}{128}\frac{L^4}{D^4} - \frac{35}{512}\frac{L^6}{D^6}\right)\frac{x^7}{D^7}$$
$$+ \left(\frac{35}{64} - \frac{105}{64}\frac{L^2}{D^2} + \frac{693}{512}\frac{L^4}{D^4} - \frac{429}{1024}\frac{L^6}{D^6} + \frac{715}{16384}\frac{L^8}{D^8}\right)\frac{x^9}{D^9} \qquad (4)$$
$$- \left(\frac{63}{128} - \frac{1155}{512}\frac{L^2}{D^2} + \frac{3003}{1024}\frac{L^4}{D^4} - \frac{6435}{4096}\frac{L^6}{D^6} + \frac{12155}{32768}\frac{L^8}{D^8}\right.$$
$$\left.\left. - \frac{4199}{131072}\frac{L^{10}}{D^{10}}\right)\frac{x^{11}}{D^{11}} + \text{etc.}\right].$$

For convenience in handling equation (4) we may indicate the coefficients of the successive odd powers of x/D by M, N, Q, S, U and W as follows:

$$M = 2,\ N = 1 - \frac{1}{4}\frac{L^2}{D^2},\quad Q = \frac{3}{4} - \frac{5}{8}\frac{L^2}{D^2} + \frac{7}{64}\frac{L^4}{D^4},$$

$$S = \frac{5}{8} - \frac{35}{32}\frac{L^2}{D^2} + \frac{63}{128}\frac{L^4}{D^4} - \frac{33}{512}\frac{L^6}{D^6},$$

$$U = \frac{35}{64} - \frac{105}{64}\frac{L^2}{D^2} + \frac{693}{512}\frac{L^4}{D^4} - \frac{429}{1024}\frac{L^6}{D^6} + \frac{715}{16384}\frac{L^8}{D^8},$$

and

$$W = \frac{63}{128} - \frac{1155}{512}\frac{L^2}{D^2} + \frac{3003}{1024}\frac{L^4}{D^4} - \frac{6435}{4096}\frac{L^6}{D^6} + \frac{12155}{32768}\frac{L^8}{D^8} - \frac{4199}{131072}\frac{L^{10}}{D^{10}}.$$

Equation (4) then becomes

$$V_0 = -\pi nI\left[M\frac{x}{D} - N\frac{x^3}{D^3} + Q\frac{x^5}{D^5} - S\frac{x^7}{D^7} + U\frac{x^9}{D^9} - W\frac{x^{11}}{D^{11}}, \text{ etc.}\right]. \qquad (5)$$

To find the potential V at a point off the axis, coördinates x, ρ, we shall make use of Laplace's equation, which for a magnetic field symmetrical about the axis of the coil, becomes [1]

[1] Mascart et Joubert, L'Elect. et le Mag. (Edit., 1896), I., p. 396.

$$\frac{\partial^2 V}{\partial x^2} + \frac{1}{\rho}\frac{\partial V}{\partial \rho} + \frac{\partial^2 V}{\partial \rho^2} = 0.$$

For points near the axis, including all points within the coil, V may be expanded in an equation of the form

$$V = V_0 + A_2\rho^2 + A_4\rho^4 + A_6\rho^6 + \text{etc.},$$

and values of A_2, A_4, etc., may be found which separately satisfy Laplace's equation. Because of symmetry, no odd powers of ρ can appear in the series.

The convergence of the series is rapid when applied to our electrodynamometer, for which the largest value of ρ is only about one fourth of R and one fifth of D.

When the values of A_2, A_4, etc., have been substituted the equation becomes

$$V = V_0 - \frac{\rho^2}{2^2}\frac{\partial^2 V_0}{\partial x^2} + \frac{\rho^4}{(2.4)^2}\frac{\partial^4 V_0}{\partial x^4} - \frac{\rho^6}{(2.4.6)^2}\frac{\partial^6 V_0}{\partial x^6} + \text{etc.} + \frac{(-1)^n \rho^{2n}}{2^{n2}\underline{n}}\frac{\partial^{2n} V_0}{\partial x^{2n}} + \text{etc.} \tag{6}$$

If the value of V_0, equation (5), is substituted in (6) we obtain:

$$\begin{aligned} V = -\pi n I \Big[& M\frac{x}{D} - N\frac{x^3}{D^3} + Q\frac{x^5}{D^5} - S\frac{x^7}{D^7} + U\frac{x^9}{D^9} - W\frac{x^{11}}{D^{11}} + \text{etc.} \\ & + \frac{3}{2}N\frac{x\rho^2}{D^3} - 5Q\frac{x^3\rho^2}{D^5} + \frac{21}{2}S\frac{x^5\rho^2}{D^7} - 18U\frac{x^7\rho^2}{D^9} + \frac{55}{2}W\frac{x^9\rho^2}{D^{11}} - \text{etc.} \\ & + \frac{15}{8}Q\frac{x\rho^4}{D^5} - \frac{105}{8}S\frac{x^3\rho^4}{D^7} + \frac{189}{4}U\frac{x^5\rho^4}{D^9} - \frac{495}{4}W\frac{x^7\rho^4}{D^{11}} + \text{etc.} \\ & + \frac{35}{16}S\frac{x\rho^6}{D^7} - \frac{105}{4}U\frac{x^3\rho^6}{D^9} + \frac{495}{4}W\frac{x^5\rho^6}{D^{11}} - \text{etc.} \\ & + \frac{315}{128}U\frac{x\rho^8}{D^9} - \frac{5575}{128}W\frac{x^3\rho^8}{D^{11}} + \text{etc.} \\ & + \frac{693}{256}W\frac{x\rho^{10}}{D^{11}} - \text{etc.} \\ & + \text{etc.} \Big] \end{aligned} \tag{7}$$

In equation (7) we may substitute the relation $\rho^2 = y^2 + z^2$, thus replacing cylindrical by cartesian coördinates. We take y horizontal and z vertical both at right angles to the axis and to x. The components of the magnetic field are

$$X = -\frac{\partial V}{\partial x}, \text{ horizontal and parallel to } x,$$

$$Y = -\frac{\partial V}{\partial y}, \text{ horizontal and parallel to } y,$$

$$Z = -\frac{\partial V}{\partial z}, \text{ vertical and parallel to } z.$$

As in our electrodynamometer, the suspended coil is always used with its axis at right angles to that of the fixed coil; we shall consider the torque of one coil on the other for this position only.

First, let us derive the expression for the torque on a single turn of the suspended coil. The equation for this turn is $x^2 + z^2 = r^2$, in which r is the radius. A conductor carrying a current tends to move across a magnetic field. The force on an element of the conductor equals the product of the strength of the magnetic field, the intensity of the current and the projection of the element on a plane normal to the field. The moment of this force, or the torque, about the axis of suspension (passing through the center of the coil) for an element whose coördinates are x, y, z, is derived as follows: The turn of effective radius r lies in a plane normal to the y axis. Assume that the element is taken in a position for which the coördinates are all positive, and that the direction of the current is taken clockwise, positive with respect to x, negative with respect to z. The products of the current and the projections of the element are: $-Idz$, for the y, z plane; $-Idz$, for the x, z plane; $+Idx$, for the x, y plane. A consideration of the magnetic field, within and due to the fixed coil, shows that it is symmetrical about the axis; that it converges for negative values of x and diverges for positive values, and that it has its largest value for the plane $x = 0$. It follows that the components of the field are all positive for a point for which x, y and z are all positive; that all the components of the torque are clockwise (looking downward), and that every element, wherever situated, wlil

give a clockwise torque, as the factors always change signs in pairs. The expression for the torque on the element (with projections dx, dz) is

$$dT_s = I[-(xX + yY)dz + xZdx]. \tag{8}$$

As $xdy = -\sqrt{r^2 - x^2}dz$, we obtain

$$dT_s = I\left[\frac{x^2X + xyY}{\sqrt{r^2 - x^2}} + xZ\right]dx. \tag{8'}$$

As the value for each quadrant is the same, the torque T_s for one term is four times the integral of (8') over one quadrant, or

$$T_s = 4I\int_{x=0}^{x=r}\left[\frac{x^2X + xyY}{\sqrt{r^2 - x^2}} + xZ\right]dx. \tag{9}$$

The torque due to the whole coil of length l and n' turns is

$$T = \frac{n'}{l}\int_{y=-\frac{l}{2}}^{y=+\frac{l}{2}} T_s dy. \tag{10}$$

Performing the operations indicated in (8') we find

$$\begin{aligned}
x^2X = \pi nI\Big\{&\frac{M}{D}x^2 - \frac{N}{D^3}\left[3x^4 - \frac{3}{2}x^2\rho^2\right]\\
&+ \frac{Q}{D^5}\left[5x^6 - 15x^4\rho^2 + \frac{15}{8}x^2\rho^4\right]\\
&- \frac{S}{D^7}\left[7x^8 - \frac{105}{2}x^6\rho^2 + \frac{315}{8}x^4\rho^4 - \frac{35}{16}x^2\rho^6\right]\\
&+ \frac{U}{D^9}\left[9x^{10} - 126x^8\rho^2 + \frac{945}{4}x^6\rho^4 - \frac{315}{4}x^4\rho^6 + \frac{315}{128}x^2\rho^8\right]\\
&- \frac{W}{D^{11}}[\text{etc.}]
\end{aligned}$$

$$\begin{aligned}
xyY = \pi nI\Big\{&\frac{N}{D^3}\left[3x^2y^2\right] - \frac{Q}{D^5}\left[10x^4y^2 - \frac{15}{2}x^2y^2(y^2 + z^2)\right]\\
&+ \frac{S}{D^7}\left[21x^6y^2 - \frac{105}{2}x^4y^2(y^2 + z^2) + \frac{105}{8}x^2y^2(y^2 + z^2)^2\right]\\
&- \frac{U}{D^9}\Big[36x^8y^2 - 189x^6y^2(y^2 + z^2) + \frac{315}{2}x^2y^2(y^2 + z^2)^2
\end{aligned}$$

$$-\frac{315}{16}x^2y^2(y^2+z^2)^3\Big]+\frac{W}{D^{11}}[\text{etc.}]-\text{etc.}\Big\}$$

$$xZ=\pi nI\Big\{\frac{N}{D^3}[3x^2z]-\frac{Q}{D^5}\Big[10x^4z-\frac{15}{2}x^2z(y^2+z^2)\Big]$$

$$+\frac{S}{D^7}\Big[21x^6z-\frac{105}{2}x^4z(y^2+z^2)+\frac{105}{8}x^2z(y^2+z^2)^2\Big]$$

$$-\frac{U}{D^9}\Big[36x^8z-189x^6z(y^2+z^2)+\frac{315}{2}x^4z(y^2+z^2)^2$$

$$-\frac{315}{16}x^2z(y^2+z^2)^3\Big]+\frac{W}{D^{11}}[\text{etc.}]-\text{etc.}\Big\}$$

For the integration indicated in equation (9) z and ρ are functions of x, ($z^2=r^2-x^2$ and $\rho^2=y^2+r^2-x^2$). Making these substitutions we obtain

$$x^2X=\pi nI\Big\{\frac{M}{D}x^2-\frac{N}{D^3}\Big[\frac{9}{2}x^4-\frac{3}{2}(y^2+r^2)x^2\Big]$$

$$+\frac{Q}{D^5}\Big[\frac{175}{8}x^6-\frac{75}{4}(y^2+r^2)x^4+\frac{15}{8}(y^2+r^2)^2x^2\Big]$$

$$-\frac{S}{D^7}\Big[\frac{1617}{16}x^8+\frac{2205}{16}(y^2+r^2)x^6+\frac{735}{16}(y^2+r^2)^2x^4$$

$$-\frac{35}{16}(y^2+r^2)^3x^2\Big]+\frac{U}{D^9}\Big[\frac{56915}{128}x^{10}-\frac{27027}{32}(y^2+r^2)x^8$$

$$+\frac{31185}{64}(y^2+r^2)^2x^6-\frac{2835}{32}(y^2+r^2)^3x^4$$

$$+\frac{315}{128}(y^2+r^2)^4x^2\Big]-\frac{W}{D^{11}}[\text{etc.}]+\text{etc.}\Big\};$$

$$xyY=\pi nI\Big\{\frac{N}{D^3}[3y^2x^2]-\frac{Q}{D^5}\Big[\frac{35}{2}y^2x^4-\frac{15}{2}y^2(y^2+r^2)x^2\Big]$$

$$+\frac{S}{D^7}\Big[\frac{693}{8}y^2x^6-\frac{315}{4}y^2(y^2+r^2)x^4+\frac{105}{8}y^2(y^2+r^2)^2x^2\Big]$$

$$-\frac{U}{D^9}\Big[\frac{6435}{16}y^2x^8-\frac{9009}{16}y^2(y^2+r^2)x^6+\frac{3465}{16}y^2(y^2+r^2)^2x^4$$

$$- \frac{315}{16} y^2(y^2+r^2)^3 x^2 \Big] + \frac{W}{D^{11}} [\text{etc.}] - \text{etc.} \Big\};$$

$$xZ = \pi n I \sqrt{r^2 - x^2} \Big\{ \frac{N}{D^3} 3x^2 - \frac{Q}{D^5} \Big[\frac{35}{2} x^4 - \frac{15}{2} (y^2+r^2)x^2 \Big]$$

$$+ \frac{S}{D^7} \Big[\frac{693}{8} x^6 - \frac{315}{4} (y^2+r^2)x^4 + \frac{105}{8} (y^2+r^2)^2 x^2 \Big]$$

$$- \frac{U}{D^9} \Big[\frac{6435}{16} x^8 - \frac{9009}{16} (y^2+r^2)x^6 + \frac{3465}{16} (y^2+r^2)^2 x^4$$

$$- \frac{315}{16} (y^2+r^2)^3 x^2 \Big] + \frac{W}{D^{11}} [\text{etc.}] - \text{etc.} \Big\}.$$

For convenience in performing the integrations, let us tabulate the values of the integrals of the form

$$4 \int_0^r \frac{x^{2n} dx}{\sqrt{r^2 - x^2}} = \frac{(2n-1)(2n-3)\cdots 3}{2n(2n-2)\cdots 4} \pi r^{2n}.$$

Value of n	1	2	3	4	5	6
Value of the integral	πr^2	$\frac{3}{4}\pi r^4$	$\frac{5}{8}\pi r^6$	$\frac{35}{64}\pi r^8$	$\frac{63}{128}\pi r^{10}$	$\frac{231}{512}\pi r^{12}$.

In the same manner for the integral

$$4 \int_0^r x^{2n} \sqrt{r^2 - x^2}\, dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2 \cdot 4 \cdot 6 \cdots (2n+2)} 2\pi r^{2n+2}$$

we obtain

Value of n	1	2	3	4	5
Value of the integral	$\frac{\pi}{4} r^4$	$\frac{\pi}{8} r^6$	$\frac{5}{64}\pi r^8$	$\frac{7}{128}\pi r^{10}$	$\frac{21}{512}\pi r^{12}$.

The integrals involving X and Y are of the former form and that involving Z is of the latter form. We obtain

$$4I \int_0^r \frac{x^2 X + xy Y}{\sqrt{r^2 - x^2}} dx = \pi^2 r^2 n I^2 \Big[\frac{M}{D} + \frac{N}{D^3} \Big(\frac{9}{2} y^2 - \frac{15}{8} r^2 \Big)$$

$$+ \frac{Q}{D^5} \Big(\frac{75}{8} y^4 - \frac{225}{16} y^2 r^2 + \frac{95}{64} r^4 \Big) + \frac{S}{D^7} \Big(\frac{245}{16} y^6$$

$$- \frac{3885}{64} y^4 r^2 + \frac{4095}{128} y^2 r^4 - \frac{1435}{1024} r^6 \Big)$$

$$+\frac{U}{D^9}\left(\frac{2835}{128}y^8-\frac{20475}{128}y^6r^2+\frac{105525}{512}y^4r^4-\frac{108675}{2048}y^2r^6\right.$$
$$\left.+\frac{22365}{16384}r^8\right)+\frac{W}{D^{11}}\left(\frac{7623}{256}y^{10}-\frac{349965}{1024}y^8r^2\right.$$
$$+\frac{832755}{1024}y^6r^4-\frac{4244625}{8192}y^4r^6+\frac{2595285}{32768}y^2r^8$$
$$\left.-\frac{45903363}{131072}r^{10}\right)+\text{etc.}\Big],$$

$$4I\int_0^r xZdx=\pi^2r^2nI^2\Big[\frac{N}{D^3}\frac{3}{4}r^2$$
$$-\frac{Q}{D^5}\left(\frac{5}{16}r^4-\frac{15}{8}y^2r^2\right)+\frac{S}{D^7}\left(\frac{105}{512}r^6-\frac{105}{32}y^2r^4\right.$$
$$\left.+\frac{105}{32}y^4r^2\right)-\frac{U}{D^9}\left(\frac{315}{2048}r^8-\frac{4725}{1024}y^2r^6\right.$$
$$\left.+\frac{1575}{128}y^4r^4-\frac{315}{64}y^6r^2\right)+\frac{W}{D^{11}}(\text{etc.})-\text{etc.}\Big].$$

Combining the above integrals we obtain the torque on a single suspended turn,

$$T_s=\pi^2r^2nI\Big[\frac{M}{D}+\frac{N}{D^3}\left(\frac{9}{2}y^2-\frac{9}{8}r^2\right)+\frac{Q}{D^5}\left(\frac{75}{8}y^4-\frac{225}{16}y^2r^2\right.$$
$$\left.+\frac{75}{64}r^4\right)+\frac{S}{D^7}\left(\frac{245}{16}y^6-\frac{3675}{64}y^4r^2+\frac{3675}{128}y^2r^4-\frac{1225}{1024}r^6\right)$$
$$+\frac{U}{D^9}\left(\frac{2835}{128}y^8-\frac{19845}{128}y^6r^2+\frac{99225}{512}y^4r^4-\frac{99225}{2048}y^2r^6\right.$$
$$\left.+\frac{19845}{16384}r^8\right)+\frac{W}{D^{11}}(\text{etc.})-\text{etc.}\Big].$$

For convenience in performing the integration indicated in (10), it is desirable to tabulate integrals of the form

$$\frac{1}{l}\int_{-\frac{l}{2}}^{+\frac{l}{2}}y^{2p}dy=\left(\frac{l}{2}\right)^{2p}\frac{1}{2p+1}.$$

Value of p	0	1	2	3	4	5
Value of the integral	1	$\frac{l^2}{12}$	$\frac{l^4}{80}$	$\frac{l^6}{448}$	$\frac{l^8}{2304}$	$\frac{l^{10}}{11264}$

We then obtain

$$T = \frac{n'}{l}\int_{-\frac{l}{2}}^{+\frac{l}{2}} T_s dy = \pi^2 r^2 n n' I^2 \left[\frac{M}{D} + \frac{N}{D^3}\left(\frac{3}{8}l^2 - \frac{9}{8}r^2\right)\right.$$
$$+ \frac{Q}{D_5}\left(\frac{15}{128}l^4 - \frac{75}{64}l^2r^2 + \frac{75}{64}r^4\right)$$
$$+ \frac{S}{D^7}\left(\frac{35}{1024}l^6 - \frac{735}{1024}l^4r^2 + \frac{1225}{512}l^2r^4 - \frac{1225}{1024}r^6\right)$$
$$+ \frac{U}{D^9}\left(\frac{315}{32768}l^8 - \frac{2835}{8192}l^6r^2 + \frac{19845}{8192}l^4r^4 - \frac{33075}{8192}l^2r^6\right.$$
$$\left.\left. + \frac{19845}{16384}r^8\right) + \frac{W}{D^{11}}(\text{etc.}) + \text{etc.}\right].$$

When the values of M, N, Q, etc., have been substituted and the expression simplified, we have

$$T = \pi^2 r^2 n n' I^2 \left[\frac{2}{D} + \frac{3}{32}\frac{1}{D^5}(4D^2 - L^2)(l^2 - 3r^2)\right.$$
$$+ \frac{15}{8192}\frac{1}{D^9}(48D^4 - 40D^2L^2 + 7L^4)(l^4 - 10l^2r^2 + 10r^4)$$
$$+ \frac{35}{524288}\frac{1}{D^{13}}(320D^6 - 560D^4L^2 + 252D^2L^4 - 33L^6)(l^6 - 21l^4r^2$$
$$+ 70l^2r^4 - 35r^6) + \frac{315}{536870912}\frac{1}{D^{17}}(8960D^8 - 26880D^6L^2$$
$$+ 22176D^4L^4 - 6864D^2L^6 + 715L^8)(l^8 - 36l^6r^2 + 252l^4r^4$$
$$\left. - 105l^2r^6 + 126r^8) - \text{etc.}\right].$$

The series expressing the value of T is rapidly convergent if l and r are small in comparison with D. Any term of the series after the first may be reduced to zero by assuming such a relation between D and L or l and r as will make one of the factors zero. The relation $D = L/2$ would make every term after the first zero, but

this relation is equivalent to saying that the diagonal ($2D$) of the coil equals its length, a relation clearly impossible, but one which is approximated when the coil becomes very long, and the field near the middle becomes nearly uniform. If $l^2 = 3r^2$ or $l = r\sqrt{3}$ the second term will vanish. If $12D^2 = 7L^2$ the next term will vanish. This relation is equivalent to $L = R\sqrt{3}$. If this relation between the length and radius of each of the two coils is chosen, the next term of the series which remains (that involving the sixth degree of l and r) is too small for consideration as are all following terms, and the series practically reduces to

$$T = \frac{2\pi^2 r^2 nn' I^2}{D} = \frac{4\pi^2 r^2 nn' I^2}{\sqrt{L^2 + 4R^2}}.$$

In deriving the formula, it has been assumed, that the coils are equivalent to current sheets. It is well to inquire whether or not this assumption may be allowed. The large (fixed) cylinder is wound with wire about 0.07 cm. diameter, including a silk insulation. The suspended cylinder is wound with a copper ribbon about .375 mm. thick and 1.25 mm. wide with spaces of approximately equal width. The cylinders are about 47 cm. and 10 cm. in diameter respectively. As the space between turns of the ribbon on the small cylinder is equal to the ribbon's width, and as the spaces on one side are diametrically opposite to a corresponding portion of the ribbon on the other side, it is evident that the average effect is that of a current sheet. We have assumed that it is proper to take as the effective diameter, the arithmetical mean between the extreme outer and inner diameters, for although the torque depends on the square of the radius for turns at various distances, we must recognize that the innermost layer of the ribbon is relatively shortened in comparison with layers further out. There is a consequent tendency to reduce the resistance and to increase the current density in the inner layers. It would seem probable therefore that the arithmetical mean diameter is fairly taken as the true mean.

The leading wires to the suspended coil might have a disturbing influence unless put in such places as to exert no torque. We provided against such torque by putting the leading wires in the plane normal to the axis of the large coil. The wires lead from

the ends of the suspended coil at opposite ends of the bottom element of the cylinder and they are carried either parallel to this bottom element or vertical, to two mercury cups (one over the other) directly below the centers of both coils. The wires to the mercury cups are twisted together, except for a short space at the cups, where of necessity they are separated. Want of symmetry here may be eliminated by reversing the connection between coils, and in our work it is always so eliminated. The winding of the fixed coil is wire of so small radius that the ripples in the magnetic field are not appreciable, and the arithmetical mean of outer and inner radius of the coil is taken for reasons similar to those mentioned in connection with the suspended coil. The leading wires to the fixed coil go to the ends of an element of the cylinder level with the axis and are twisted together except for a piece parallel and near this element. The latter wire can produce no torque about a vertical axis. Errors due to the effect of the earth's magnetic field are avoided by reversing the current through the whole instrument. For a set of observations the four possible permutations of current through the two coils are taken. The resulting average is practically free from errors due to asymmetry and stray fields.

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ON THE THEORY OF THE ELECTROLYTIC RECTIFIER.

BY S. R. COOK.

IN the PHYSICAL REVIEW for January, 1904, in a paper with the above title, I showed that the very high apparent resistance of the aluminum electrolytic rectifier was due to a counter electromotive force. This counter electromotive force, as well as the direct electromotive force was measured, in my former paper, by a Weston voltmeter. Although the voltmeter was accurate to less than one per cent. the time required, for the needle to attain to its reading and the inertia of the moving system, introduced into the readings, however carefully taken, certain unavoidable errors which could not be accurately computed. These errors, especially the time that elapsed between the breaking of the connections for the applied electromotive force and the making of the connections for measuring the counter electromotive force, tended to reduce the measured value of the counter electromotive force; the measurements obtained showed that from eighty-five to ninety-five per cent. of the apparent resistance could be accounted for as due to counter electromotive force.

These measurements were thought to be sufficiently approximate to give good reason for believing that the entire resistance except that due to the electrolytic resistance of the cell, was due to a counter electromotive force. It was thought that if the counter electromotive force could be measured immediately after breaking the electrolyzing current, that it would account for the entire apparent resistance. In order to measure the counter electromotive force immediately after the current was broken, a pendulum was constructed for making and breaking currents at definite intervals. The pendulum was of the usual type; being, however, constructed entirely of metal it was especially heavy and suited to precision measurements. The bob was so adjusted that the time of vibration was very approximately one second.

Apparatus.

The apparatus consisted of the electrolytic rectifier, made up as described in my former paper, an accumulator of twenty-eight cells, a Weston ammeter, milliammeter, and voltmeter, a standard condenser, a ballistic galvanometer, and the pendulum with keys and pole-changers as indicated in the diagram (Fig. 1). The ballistic galvanometer was so sensitive to the high potential necessary to the measurements, that it was found convenient to shunt it through a resistance of 50 ohms. This not only brought the deflection of the mirror within the range of the scale, but made the swing of the needle nearly aperiodic. The effect of this on the readings will be noted later.

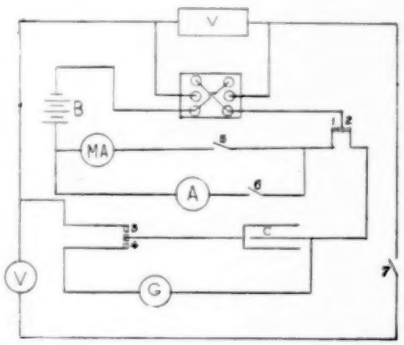

Fig. 1.

Keys 1, 2, 3 and 4 could be used to either make or break the current by means of the pendulum or they could be permanently closed: keys 5, 6 and 7 were closed only when measurements were to be made.

Data.

The measurements desired were: the direct electromotive force, applied to the electrolytic rectifier; the counter electromotive force given by the electrolytic cell immediately after the current was broken; and the value of the current through the electrolytic rectifier, while the applied electromotive force was effective.

In order to determine the direct E.M.F. applied to the electrolytic rectifier key 1 was closed. The pendulum was then released, closing key 2 and allowing the condenser to be charged, through key 3, at the potential of the electrolytic rectifier, and then discharging the condenser through the galvanometer by closing key 4 after opening key 3. The potential due to the direct applied E.M.F. could also be measured independently by the voltmeter *V*. The counter E.M.F. of the electrolytic cell v was measured in the same manner as the applied E.M.F. by allowing the pendulum to first open key 1 and at the same time close key 2. The other opera-

tions were identical with those for the determination of the applied E.M.F.

It is evident that the condenser was charged at the potential of v when key 3 was opened. The time elapsing between the opening of key 1 and the opening of key 3 was kept constant throughout the entire series of measurements and was very approximately .01 second.

The above determinations were made for three temperatures. These temperatures were similar to those in my former paper and set forth the action of the electrolytic rectifier at the three points of greatest scientific and practical interest.

Measurements of the applied E.M.F. current, and counter E.M.F., for the temperatures 0.5° 18°, and 50° respectively are exhibited in the following tables:

TABLE I.

Temperature 0.5°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Effective E.M.F.	Electrolytic Resistance.
4.30	.0012	4.14	0.16	123
8.60	.0020	8.32	0.28	140
13.20	.0040	12.52	0.64	170
17.64	.0075	16.80	0.84	112
22.12	.0090	20.88	1.24	132
26.74	.0100	25.20	1.54	154
31.44	.0110	29.40	2.04	185
36.00	.0160	33.16	2.84	177
40.52	.1100	30.32	10.20	93
43.88	1.5000	24.56	19.32	12.8

TABLE II.

Temperature 18°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Effective E.M.F.	Electrolytic Resistance.
4.48	.0012	4.36	0.12	100
8.93	.0022	8.64	0.29	163
13.56	.0180	12.46	1.10	61
18.32	.0220	16.48	1.84	64
22.76	.0260	20.36	2.40	92
27.41	.0280	24.48	2.93	101
32.00	.7500	21.82	10.18	13
32.80	1.6500	20.16	12.64	7.6

TABLE III.

Temperature 50°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Effective E.M.F.	Electrolytic Resistance.
4.80	.0025	4.56	0.24	96
8.69	.0080	7.72	0.98	121
13.04	.1500	10.45	2.59	17.3
17.70	.2000	13.31	4.39	21.9
21.52	.2250	16.36	5.16	23
26.40	.2700	19.60	6.80	25
29.40	.3500	20.52	8.78	25
31.36	1.9000	18.16	13.20	7

The data from these tables are exhibited by the curves in Figs. 2, 3 and 4 so far as 30 volts, or where the film of alumina begins to crystallize. Fig. 5 contains the complete curves exhibiting all the data in the three tables. Curves 1 and 2, in each of Figs. 2, 3 and 4, show the relation of the applied and counter electromotive force to the current. In Fig. 5 curves I., II. and III. show the re-

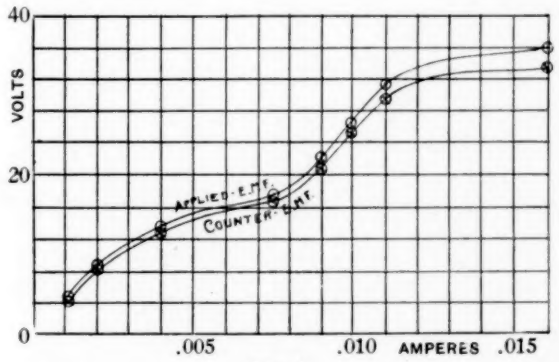

Fig. 2.

lation of the applied electromotive force, and curves I′., II′. and III′. the relation of the counter electromotive force to the current.

Accuracy Attained. — In my former paper about 85 per cent. of the apparent resistance was accounted for by the counter electromotive force measured. The object of redetermining the value of the counter electromotive force, at a shorter interval of time after the applied current was broken, and by a more accurate method was to

show if possible that all the apparent resistance was due to counter electromotive force.

The use of the ballistic galvanometer assures the measurement of both the direct and counter electromotive forces independent of the ohmic resistance of the electrolytic rectifier; and if we can assume that in a shunted ballistic galvanometer the deflection of the needle

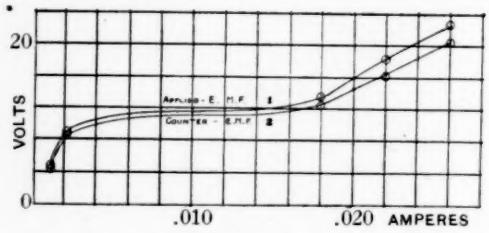

Fig. 3.

is directly proportional to the current passing through the galvanometer, the reading of the galvanometer will give the true potential of the cell. Stewart[1] has shown that for a damped ballistic galvanometer

$$\theta = KQ.$$

Where θ is the angle of the deflection of the needle, Q quantity of electricity discharged through the galvanometer, and K is a constant

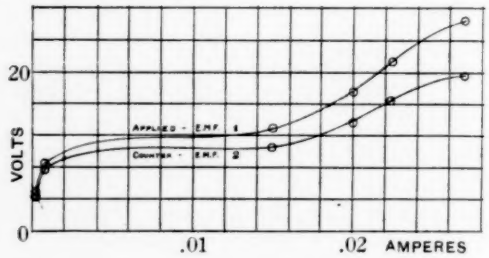

Fig. 4.

depending on the damping system. As the damping system, *i. e.*, the shunt of the galvanometer — was not changed during the entire set of measurements, K was constant and the galvanometer gave the true potential. This was tested by reading the direct potential from the voltmeter and comparing the results with the potentials obtained

[1] PHYSICAL REVIEW, Vol. XVI., 1903.

from the readings of the ballistic galvanometer. When the two sets of readings, taken at 18°, were compared, it was found that the average variation was .008, or less than 1 per cent., which is not greater than the least reading of the voltmeter. Since we are only concerned with the relative potentials, and as in a large majority of measurements the difference between the direct and counter E.M.F. is less than 1 per cent. of the total E.M.F., the error in the determination of the potential by a shunted ballistic galvanometer being less than one tenth of one per cent. may be neglected.

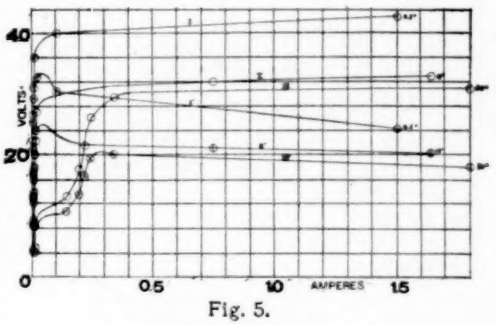

Fig. 5.

The only other error worthy of remark was that due to the decay of the counter E.M.F. during the interval between breaking the polarizing current and charging the condenser. As this interval was short, being not more than .01 second; and the decrease of the counter E.M.F. from its maximum value during this interval, was very small, as will be seen from the curve of decay, to be given presently; this error could not have been more than two or three tenths of one per cent. So that the total error was probably less than one per cent.

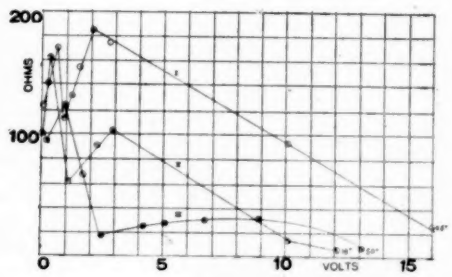

Fig 6.

Decay of the Counter Electromotive Force.

In order to show that the measured counter electromotive force was very approximately the value of the counter electromotive force under the specific conditions, I determined the decay of the counter electromotive force with time; from which by extrapolation the maximum counter E.M.F. might be computed.

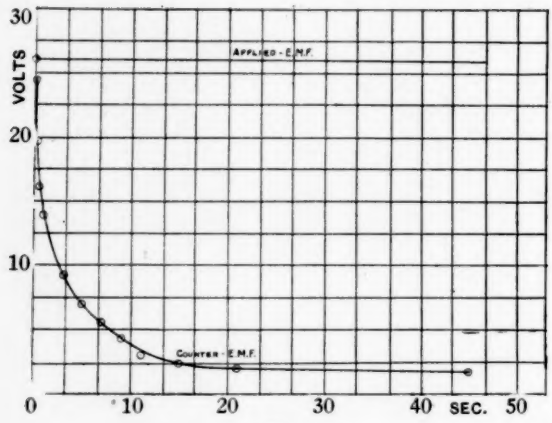

Fig. 7.

Table IV. exhibits the results obtained, and Fig. 7 exhibits the curve showing the relation between the counter E.M.F. and time after breaking the current.

TABLE IV.

Direct E. M. F. 26 *Volts.*

Time in Seconds.	Counter E.M.F. Volts.	Time in Seconds.	Counter E.M.F. Volts.	Time in Seconds.	Counter E.M.F. Volts.
.01	24.64	3.00	8.96	11.00	2.98
.42	19.30	5.00	6.88	15.00	2.49
.68	15.77	7.00	5.64	21.00	2.08
1.00	14.04	9.00	4.32	51.00	1.92

DISCUSSION OF THE DATA.

From a study of the data in Tables I., II. and III. and the corresponding curves it will appear that the counter electromotive force completely accounts for the high apparent resistance of the electrolytic rectifier. This will be made clear by a study of the first three columns in the tables. It will be observed that the effective electromotive force, as exhibited in the fourth column of the table is, with low voltage, very small, and increases with the increase of the current. The fifth column designated "Electrolytic Resistance" includes the electrolytic resistance of the electrolyte and the ionic resistance of the film: that is, all resistance offered to the ionic

transfer of the current. It may be remarked that this total ionic resistance increases at first with the potential difference, then suddenly decreases and again increases to a second maximum, and then falls off rapidly as the crystallization of the film exposes the free metallic surface to the charged ions (Fig. 6).

In my former paper I showed that the final decrease of the resistance of the film was due to the crystallization of the alumina and the exposure of the free metallic aluminum to the charged ions. The cause for the first decrease in the resistance is not so evident, but I believe it to be due to some physical or possibly physical and chemical change of the film. It is quite apparent that when the film is formed under low potentials, it is composed of a white amorphous substance: and that when the potential is increased, the film becomes harder and more granular in structure, though not yet crystalline: and that when the potential reaches a certain critical value, depending on the temperature of the solution, the film crystallizes in very hard black crystals, which have every appearance of emery. It seems quite probable that this first change of the physical state of the film produces a condition that would give a greater freedom to the transmission of the ions through the film, and hence decrease the total resistance.

On the Theory.

The experimental data already obtained by my own investigations and those of others seem to justify the following remarks on the possible theory of the electrolytic rectifier.

Whenever oxygen is the primary or secondary product of the anion, the aluminum anode is covered with a film of hydroxide which has a very high resistance,[1] so high indeed that it acts as a dielectric to the charge on the ions. This non-conducting film between the metallic aluminum and the electrolyte produces a condenser effect with the negative charge on the anions of the electrolyte.

The conditions then that always exist, when a direct current is applied to an electrolytic rectifier with a well-formed aluminum anode are: (1) When any potential less than the critical potential

[1] W. R. Mott. Electro-chem., Ind., N. Y., 2, pp. 352–355, September, 1904.

is applied to the electrodes there is induced an equal and opposite charge in the electrolyte next to the respective electrodes. (This is on the assumption that the film acts as a perfect dielectric.) (2) When the current is broken there exist bound charges in the electrolyte and on the electrodes. These bound charges on the electrodes, which may be assumed to be equal to the bound charges in the electrolyte, are what produce the counter electromotive force. The curve of decay shows the rate at which these charged ions pass through the film and give up their charge to the metallic plate. (3) When the current is reversed the hydrogen ions pass through the film more readily than the oxygen or other negative ions, forming a gas between the metallic aluminum and the film, thus breaking away the film and exposing the metal to the charged ions. (4) When an alternating current is applied the film acts as a semipermeable membrane. The hydrogen atoms having less mass and greater velocity than the oxygen or other negative ions pass through much more freely than the more slowly moving anions. (5) The critical potential value for an electrolytic rectifier depends upon the electrolyte used and the temperature of the cell. When the critical potential has been passed, the film crystallizes and in crystallizing exposes the metallic aluminum. The crystallization continues so long as the potential is kept above the critical value.

SUMMARY OF RESULTS AND CONCLUSIONS.

1. From results obtained both in this and my former paper it may be concluded that the high apparent resistance of the electrolytic rectifier, when aluminum is the anode, is due to the counter electromotive force produced by the difference in charge of the cations around the carbon plate and that of the anions around the aluminum plate.

2. So long as the potential is below the critical value the resistance of the film to the transfer of electricity is such that very few of the anions pass through it.

3. When the aluminum is the kathode hydrogen forms between the metallic aluminum and the film; this breaks the film and exposes metallic aluminum, thus allowing only a small polarization and hence a low resistance.

4. It has been shown that there exist two potentials, depending on the temperature, at which the film of aluminum undergoes a change such that its resistance to the passage of the ions is decreased, the first being at a potential whose value is about one-third the value of the second. The second is at the critical value of the potential and is due to the crystallization of the film.

In conclusion I wish to thank Professor Dayton C. Miller, of Case School of Applied Science, at which place the work was carried out, for generous assistance in furnishing general and specific apparatus for carrying on the work.

PHYSICAL LABORATORY, CORNELL UNIVERSITY,
November 25, 1904.

THE CONDUCTION LOSSES FROM CARBON FILAMENTS WHEN HEATED TO INCANDESCENCE IN VARIOUS GASES.

BY L. W. HARTMAN.

THE data incorporated in this paper were obtained by the author during a more extended investigation on the energy lost through conduction and convection from incandescent platinum filaments in air. This work naturally suggested a similar investigation on the filament of the incandescent lamp when it was surrounded by gases of different conductivities. In all, three different gases were used, viz., hydrogen, nitrogen and carbon dioxide.

The following method was utilized. An incandescent lamp with a straight filament was mounted in front of a platinum oven. The interior of the latter contained a piece of magnesium oxide enclosing a thermo-element, the terminals of which were connected directly to a Kaiser & Schmidt millivoltmeter. The current through the lamp and the voltage at the terminals of the lamp, were determined at every observation; from these readings the power supplied to the filament was computed. When the interior of the oven was heated, its temperature could be determined from the electromotive force generated in the thermo-element. The values of the electromotive force generated at different temperatures in a platinum, platinum-rhodium thermo-element were taken from the table cited by Kohlrausch.[1] The incandescent lamp was then placed directly in front of the oven so that on looking through a telescope placed at some distance from the oven and pointed toward its interior, one could see the filament of the lamp against the magnesium oxide as a background. When both were heated to a high temperature the appearance of one was not in general the same as that of the other. When the current through the lamp was varied, however, a value was finally attained where the filament, when viewed through the telescope, apparently vanished. At this point it was assumed that the

[1] Lehrbuch der Praktischen Physik, p. 157, 1901, 9te Aufl.

filament and the magnesium oxide were at the same temperature. The power supplied to this lamp, which for convenience may be called the standard lamp, was thus determined for temperatures varying from 800°–1600° C. This lamp was then calibrated several times, and corrections for the absorption of the glass were always made.

An unexhausted incandescent lamp of small size was then placed on the mercury pump and exhausted until a good vacuum was obtained. Hydrogen, generated in a Kipp generator, was then passed through a succession of wash bottles and drying agents before it was allowed to enter the lamp. The first wash bottle contained water to absorb any hydrochloric acid carried over mechanically by the gas; the next two bottles contained concentrated sulphuric acid which absorbed traces of water; the gas was next passed through drying tubes containing calcium chloride; and lastly through a tube of soda lime, from which the gas could be passed into the lamp. The drying apparatus was connected directly to the lamp and to the pump by means of a glass Y provided with a ground glass stopcock in its stem. One arm of the Y led to the pump; the other arm led to the lamp which was to be filled with dry gas. After the lamp had been completely exhausted it was allowed to fill slowly with dry hydrogen. Then it was again exhausted and refilled with the same gas several times in succession. At last when the lamp was filled with dry hydrogen under atmospheric pressure, it was carefully sealed off.

This lamp was then connected in an electric circuit and mounted in front of the standard lamp so that the filaments of the two lamps as seen through the telescope appeared coincident, the one superimposed upon the other. The current passing through the lamp filled with the given gas was then varied until its filament, as seen against the background formed by the incandescent filament of the standard lamp, apparently vanished from the field of view.

Readings of the current in each lamp were thus taken for different degrees of incandescence. The standard lamp was then similarly mounted in front of the lamp filled with hydrogen and these observations were repeated. To eliminate the absorption of the glass, the energy-temperature curves of the lamp filled with hydro-

gen were plotted for both these positions, and then the mean values of these two curves were taken as the values of the power supplied to the lamp at a given temperature.

These measurements having been completed, the lamp was unsealed and mounted on the mercury pump, after which it was exhausted and filled with dry carbon dioxide. This gas, obtained by the action of hydrochloric acid on calcium carbonate in an ordinary carbon dioxide generator, was successively passed through water, concentrated sulphuric acid and lastly through several drying tubes filled with calcium chloride. Before again sealing off, the lamp was exhausted and filled with this gas several times in succession.

The lamp, now filled with carbon dioxide, was then mounted in front of the standard lamp as above. Observations with increasing temperatures were then made, with as much care and rapidity as were consistent with accuracy. Suddenly the filament burned out. This was not an unexpected result, although all the necessary precautions had been taken to defer this event as long as possible.

It is known that at ordinary temperatures carbon dioxide dissociates very slightly, and with increasing temperature the degree of dissociation increases rapidly. At 600°C. the dissociation is fairly marked, and at 1000°–1200°C. the gas dissociates rapidly into carbon monoxide and oxygen according to the equation

$$2CO_2 \rightleftharpoons 2CO + O_2.$$

At first it was thought that this reaction took place and that the oxygen united with carbon at a high temperature in the presence of an excess of carbon monoxide to form either carbon dioxide or else more carbon monoxide. This view, however, proved to be incorrect. The reaction between carbon and carbon dioxide at high temperature has been shown by Boudouard[1] to proceed according to the equation

$$CO_2 + C = 2CO.$$

A chemical reaction here, therefore, was to be expected. A second lamp was then exhausted and filled with carbon dioxide, and these observations were repeated as rapidly as possible. This time a

[1] Boudouard, C. R., **128**, 824, 1899.

temperature approximating 1550°C. was attained before the carbon burned off.

As in the first case, a third lamp was now filled with dry hydrogen and a series of observations were made upon it. The lamp was then unsealed, exhausted, and filled with nitrogen. The same series of observations were again repeated with the lamp now filled with an atmosphere of nitrogen. To get pure nitrogen, a mixture of potassium nitrate and ammonium chloride were dissolved in water and then heated for a time upon a sand bath over a Bunsen burner until a generous evolution of gas took place. This gas was allowed to escape into the air until one felt assured that all the air had been expelled from the generating flask, when the gas was collected in a suitable receiver over water. The reaction between the salts above mentioned is the one commonly employed in obtaining nitrogen from the nitrates, and is indicated in the following equation :

$$KNO_2 + NH_4Cl = 2N + 2H_2O + KCl.$$

To be certain that all traces of oxgen were removed before the gas was allowed to enter the lamp, it was first passed through two wash bottles containing a fresh solution of alkaline pyrogallol,[1] and then through the series of drying reagents used in the case of hydrogen, viz., concentrated sulphuric acid, calcium chloride and soda lime. A mere trace of hydrogen was admitted into this gas to combine with possible traces of oxygon which might still be present. The lamp was then thoroughly exhausted and refilled with this gas several times in succession, after which the lamp was sealed off with the contained nitrogen at atmospheric pressure.

After the necessary observations on the filament inclosed within this gas had been completed, the seal was again broken and the nitrogen pumped out. When a high vacuum was obtained, the lamp was again sealed off and the temperature-energy measurements were repeated as before.

These measurements having been completed, the carbon of each lamp was removed and the length and cross section of the filaments were determined. Then the watts per centimeter length sup-

[1] Hempel, p. 149, 1902, 3d Ed.

plied to each filament were computed for the particular gases used in each lamp. Using these values for abscissæ and corrected temperatures for ordinates the curves for lamp III., shown in Fig. 1, were plotted. These curves show in a graphic way the watts per

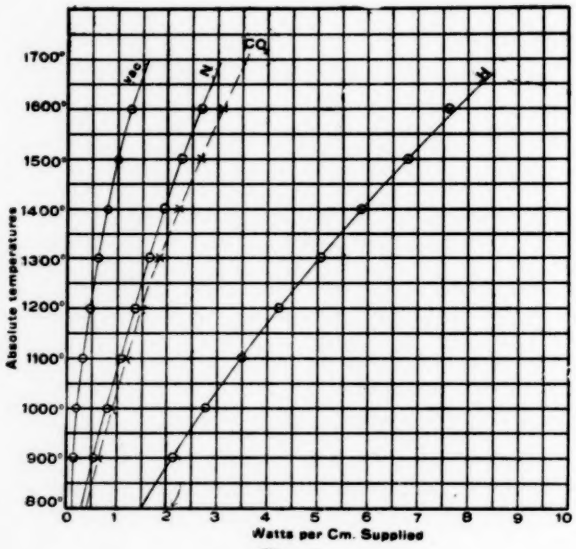

Fig. 1.

cm. length supplied to a filament in order to produce a given temperature when it is surrounded by the different gases indicated.

Knowing the dimensions of each filament, the watts per centimeter length required to supply the energy radiated at a given temperature can be computed by means of the formula

$$W = \frac{Cs}{k}(T^4 - t^4)$$

where W is the energy in Watts, C[1] for a black body is equal to 1.28×10^{-12} referred to sq. cm., second, and water-grm. calorie, and k is equal to one watt expressed in water-grm. calories per sec.,[2] viz., 0.239, and s is equal to the surface in sq. cm. Reduced to its simplest form, therefore,

$$W = 5.55 \times 10^{-12} s(T^4 - t^4)$$

[1] Kohlrausch, loc. cit., p. 313.

[2] Ibid., p. 604.

where T and t are respectively the temperature of the black body and the temperature of the room expressed in absolute degrees. It is evident that in these computations the assumption is made that carbon behaves like a black body. This may not be strictly true, but the assumption serves as the basis of some interesting results.

If, for a given temperature, these computed values of watts per centimeter length be subtracted from the values of the watts required by the filaments in the different gases, the value of the loss at the given temperature, due to conduction in the different gases, can be determined. These values are tabulated in section three of Table I. The differences for the filament in a vacuum, given in this section of Table I., are negative; since the values for the most part are exceedingly small, this discrepancy may be ascribed to errors in measurement, or to the fact that this carbon is a better radiator than a black body. If the latter assumption is true, one would expect to get negative values here. This possibility is suggested by some earlier work on the radiation from the carbon filament of the incandescent lamp.[1] For the sake of comparison, the energy losses at 1200° are arbitrarily taken as unity and the relative losses at other temperatures are computed. These results are given in the last section of Table I. Knowing the dimensions of the carbon filaments, energy relations similar to those mentioned, referred to the square millimeter as the unit surface, are computed from Table I. and these are tabulated in Table II.

With reference to the values for carbon dioxide in the case of lamp III., one should note that these losses are computed. If the gases, hydrogen and nitrogen, under atmospheric pressure be introduced in succession in two given lamps and the energy losses were determined as indicated above, it seems reasonable to assume that at a given temperature the ratio of the energy losses in hydrogen and nitrogen in one lamp will be the same as the ratio of the losses in the second lamp; or, if we indicate the losses in the first lamp by L_H' and L_N', the subscripts referring to the gas, and the losses in the second lamp by L_H'' and L_N'', we can express the relation thus:

[1] Nichols, PHYS. REV. II., 260, 1895.

$$L_H' : L_N' = L_H'' : L_N''.$$

Because of the chemical behavior of carbon dioxide in the presence of carbon, as above noted, it was deemed best not to introduce this gas in lamp III.; the principle just mentioned, therefore, was utilized to determine the losses from the filament of this lamp in an atmosphere of carbon dioxide. The loss at any given temperature, therefore, may be assumed to be

$$L_{CO_2}''' = \frac{L_{CO_2}'' \cdot L_H'''}{L_N''}$$

where L is the loss in watts in the gas concerned. The primes refer to the number of the lamp and the subscripts to the gases enclosed in the lamp. The losses for carbon dioxide, given in section three of Table I., are computed thus.

In section two of this table, the values of the watts supplied to lamp III. for carbon dioxide at a given temperature, is equal to the sum of the two values, corresponding to the same gas and temperature, given in sections one and three of the same table. Because of the chemical reaction which takes place, it is almost certain that these values do not represent the true losses from a filament into an atmosphere of carbon dioxide. On the contrary there is a combination of the losses into an atmosphere of carbon monoxide, or an atmosphere composed of varying proportions of carbon monoxide and carbon dioxide, together with the heat of reaction between the carbon dioxide and carbon. The data obtained for carbon dioxide, therefore, are of questionable value. The data obtained with nitrogen and hydrogen, however, are probably near the truth.

In a recent article,[1] where the conduction losses from hot platinum filaments in air were computed, the author used the formula

$$W_L = k\left(1 + \frac{\alpha T}{2}\right) T.$$

At that time it was suggested that the values obtained from this formula were in all probability not exact, because an extrapolation of this formula to the values of temperature there attained was scarcely justifiable. Taking this formula, however, and substituting

[1] Hartman, Phys. Zeitschr., 5, 579, 1904.

the constants which have been determined for hydrogen and nitrogen [1] the energy losses due to conduction in these gases were computed for lamp III. It was noted that these values were uniformly larger than the observed values. To my surprise, when the ratios of the computed to the observed values were determined, these were found to be practically constant, as is shown by the following table:

Watts per cm. Length Lost in Lamp III. for the Following Absolute Temperatures.

Gas.	Temperature =	900°	1000°	1100°	1200°	1300°	1400°	1500°
H	Watts computed = *W*	3.70	4.61	5.59	6.66	7.81	9.05	10.40
H	Watts observed = *L*	1.97	2.51	3.11	3.70	4.28	4.89	5.46
H	Ratio of *W*: *L*	1.88	1.84	1.80	1.81	1.83	1.85	1.90
N	Watts computed = *W*	0.54	0.67	0.82	0.97	1.14	1.31	1.51
N	Watts observed = *L*	0.42	0.56	0.70	0.82	0.90	0.95	0.96
N	Ratio of *W*: *L*	1.28	1.20	1.17	1.18	1.27	1.39 (?)	1.57 (?)

When these observations were taken, the limited time at my disposal made an extensive investigation impossible; yet these data, although meager, seem to show conclusively that at any given temperature within the range heretofore specified, the energy losses can be computed with a fair degree of accuracy simply by the introduction of a constant in the formula last mentioned. If, therefore, the losses in hydrogen, computed from this formula, be divided by 1.85, the results will be approximately the same as the observed losses. This is true of both lamp No. II. and lamp No. III. In case of lamp No. III., if the computed values for the filament in an atmosphere of nitrogen, be divided by 1.25, values very closely approximating the observed energy losses will be obtained. This is true for temperatures extending from 1000° to 1500° absolute.

If, therefore, the computed losses in hydrogen and nitrogen at the temperatures above mentioned, are corrected by introducing these constants, the ratio of the computed loss in hydrogan for a given temperature to the computed loss in nitrogen for the same temperature can be determined. These ratios are given in the first part of the following table. The same ratios between the observed values of the losses in hydrogen and nitrogen are given in the second part of the following table:

[1] Cf. Nernst, Boltzmann Festschrift, p. 912, 1904; Meyer, Kinetic Theory of Gases, p. 294, 1899, 2d Ed.; Wüllner, Lehrbuch der Experimentalphysik, 2, 574, 1896, 5te Aufl.

Temperature =	900°	1000°	1100°	1200°	1300°	1400°	1500°
Ratio of $W_H:W_N$.....	4.55	4.55	4.55	4.55	4.55	4.55	4.55
Ratio of $L_H''':L_N'''$.....	4.70	4.48	4.45	4.51	4.75	5.20?	5.70?

These two sets of values are in as close agreement as one could expect from this type of measurement.

TABLE I.

Lamp No.	Diameter of filament.	Absolute Temperatures. 900°	1000°	1100°	1200°	1300°	1400°	1500°	1600°
		Energy in watts per cm. length for the above temperatures (computed from Stefan's Law).							
I.	0.011cm.	0.123	0.187	0.273	0.387	0.533	0.717	0.946	1.224
II.	0.0185 "	0.204	0.311	0.456	0.645	0.888	1.195	1.575	2.040
III.	0.0157 "	0.173	0.264	0.387	0.548	0.754	1.014	1.340	1.730
	Gases.	Watts per cm. supplied at above temperatures for the following gases.							
I.	H	2.08	2.63	3.18	3.83	4.47	5.15	5.95	6.88
I.	CO_2	0.61	0.77	0.985	1.235	1.53	1.835	2.18	2.54
II.	CO_2	0.885	1.10	1.363	1.690	2.06	2.480	2.94	3.42
III.	H	2.14	2.77	3.50	4.25	5 03	5.90	6.80	7.56
III.	N	0.595	0.82	1.09	1.37	1.65	1.96	2.30 (?)	2.70 (?)
III.	CO_2	0.66	0.86	1.15	1.45	1.84	2.24	2.69	3.12
III.	Vacuum.	0.145	0.18	0.325	0.47	0.615	0.81	1.03	1.28
		Watts per cm. lost through conduction.							
I.	H	1.96	2.44	2.91	3.44	3.94	4.43	5.00	5.68
I.	CO_2	0.49	0.58	0.71	0.84	1.00	1.11	1.23	1.32
II.	CO_2	0.69	0.79	0.90	1.04	1.17	1.28	1.36	1.38
III.	H	1.97	2.51	3.11	3.70	4.28	4.89	5.46	5.83
III.	N	0.42	0.56	0.70	0.82	0.90	0.95	0.96 (?)	0.97 (?)
III.	CO_2	0.49	0.59	0.76	0.90	1.00	1.23	1.35	1.39
III.	Vacuum.	−0.03	−0.08	−0.06	−0.08	−0.14	−0.20	−0.31	−0.45
		Ratio of heat loss per cm. length, assuming loss at 1200° = 1.00.							
I.	H	0.570	0.710	0.845	1.00	1.15	1.29	1.45	1.64
I.	CO_2	0.585	0.670	0.845	1.00	1.19	1.32	1.47	1.57
II.	CO_2	0.665	0.760	0.865	1.00	1.18	1.23	1.31	1.33
III.	H	0.532	0.680	0.840	1.00	1.16	1.32	1.48	1.57
III.	N	0.513	0.680	0.860	1.00	1.10	1.14	1.17 (?)	1.19 (?)
III.	CO_2	0.545	0.660	0.840	1.00	1.20	1.36	1.50	1.54

It may be noted in passing that values of K and W for both hydrogen and nitrogen were computed from the formulæ

$$K = k(1 + aT)$$

and $W = k(1 + aT)T$, where K stands for the conductivity, W is the energy lost through conduction, T is the temperature difference between the filament and its surroundings, and k and a are constants for the gas concerned. For hydrogen[1] $k = 3.5 \times 10^{-4}$ and $a = 24 \times 10^{-4}$. The resulting values, for temperatures ranging

TABLE II.

Lamp No.	Gases.	Absolute Temperatures. = 900°	1000°	1100°	1200°	1300°	1400°	1500°	1600°
		Watts per sq. mm. for the above temperatures (computed from Stefan's Law).							
I		0.0351	0.0536	0.0784	0.111	0.153	0.206	0.271	0.350
II.		0.0351	0.0535	0.0784	0.111	0.152	0.206	0.270	0.351
III.		0.0352	0.0535	0.0785	0.111	0.153	0.206	0.272	0.351
		Watts per sq. mm. supplied at above temperatures for the following gases							
I.	H	0.596	0.755	0.912	1.100	1.280	1.480	1.710	1.970
I.	CO_2	0.176	0.221	0.282	0.354	0.439	0.575	0.625	0.730
II.	CO_2	0.152	0.189	0.244	0.290	0.354	0.426	0.505	0.590
III.	H	0.435	0.560	0.710	0.862	1.020	1.200	1.380	1.520
III.	N	0.120	0.167	0.222	0.278	0.334	0.396	0.466(?)	0.548(?)
III.	CO_2	0.134	0.174	0.233	0.294	0.373	0.455	0.545	0.626
III.	Vacuum.	0.029	0.037	0.066	0.096	0.125	0.163	0.202	0.256
		Watts per sq. mm. lost at above temperatures through conduction.							
I.	H	0.563	0.700	0.835	0.986	1.13	1.270	1.430	1.625
I.	CO_2	0.140	0.166	0.204	0.240	0.286	0.318	0.353	0.378
II.	CO_2	0.119	0.136	0.155	0.179	0.202	0.220	0.234	0.238
III.	H	0.400	0.510	0.630	0.750	0.870	0.990	1.110	1.180
III.	N	0.085	0.114	0.142	0.164	0.183	0.190	0.193(?)	0.199(?)
III.	CO_2	0.099	0.120	0.155	0.182	0.210	0.250	0.274	0.276
III.	Vacuum.	−0.006	−0.016	−0.012	0.016	0.028	−0.038	0.057	0.091
		Ratio of heat loss per sq. mm., assuming loss at 1200° = 1.00.							
I.	H	0.570	0.710	0.846	1.00	1.15	1.29	1.45	1.65
I.	CO_2	0.584	0.690	0.850	1.00	1.19	1.32	1.47	1.58
II.	CO_2	0.665	0.760	0.866	1.00	1.13	1.23	1.31	1.33
III.	H	0.534	0.680	0.840	1.00	1.16	1.32	1.48	1.57
III.	N	0.519	0.695	0.866	1.00	1.12	1.16	1.18 (?)	1.20 (?)
III.	CO_2	0.545	0.660	0.852	1.00	1.15	1.37	1.51	1.52

between 900° and 1500° absolute, were treated as in the above table and a wide variation in the ratio values was found to exist.

[1] Meyer, loc. cit.

From these computations, therefore, it would appear that the last two expressions do not express the conductivity and energy losses for temperatures ranging between 700° and 1300°C., although between 0° and 100°C., the conductivity of hydrogen is commonly expressed,[1] as above indicated, by the expression,

$$K_H = 3.5(1 + 0.0024T)10^{-4}.$$

For temperatures ranging from 700° — 1200°C., however, the energy losses in hydrogen are expressed fairly accurately by

$$W = \frac{3.5}{1.85}\left(1. + 0.0024\frac{T}{2}\right)T$$

$$= 1.89(1 + 0.0012T)T, \text{ where}$$

T is the difference in temperature between the filament and its surroundings. In this series of measurements, as was found in a previous investigation by the writer, the energy loss seems to be quite independent of the cross-section of the filament. This is seen by a reference to Table I.

When the above work was performed a lack of time made a more extended investigation impossible. This paper, therefore, is merely preliminary to a more extended investigation with other gases. In conclusion, for the apparatus loaned and the courtesies extended, the writer wishes to acknowledge his indebtedness to Prof. W. Nernst in whose laboratory this work was performed.

[1] Meyer, loc. cit.

AN OPTICAL DETERMINATION OF THE ZERO POINT IN THE TELESCOPE-MIRROR-SCALE METHOD.

By A. de Forest Palmer, Jr.

When a telescope, mirror, and scale have been properly adjusted, for the purpose of measuring angular deflections, a plane containing the axis, about which the mirror turns and normal to the plane of the scale intersects the line of the graduations at the true zero point from which the deflections should be reckoned. In practice it is customary to bring the central scale division into coincidence with this point by turning the scale in a plane normal to the axis until its extreme divisions are equidistant from the axis. It has been proved by Holman,[1] who gives a very complete discussion of the sources of error involved in the telescope-mirror-scale method and of the precision with which the various adjustments must be carried out, that the difference between these distances must not exceed six tenths of a millimeter when the scale distance is one meter and angular deflections are to be determined within one tenth of one per cent. In many cases, owing to the disposition of the apparatus or the inaccessibility of the axis, the attainment of this degree of accuracy is very difficult, if not impossible.

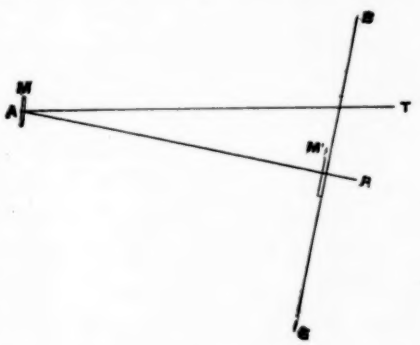

Fig. 1.

When the mirror is sufficiently steady to allow accurate scale readings the zero point can be easily determined, within the required limits, by an optical method free from the above difficulties. The

[1] S. W. Holman, "The Telescope-Mirror-Scale Method; Adjustments and Tests," published in 1898 by John Wiley & Sons, New York.

plan of the method is illustrated, diagrammatically, in Fig. 1, where TA represents the optic axis of the telescope, SS the line of the graduations of the scale, M the mirror, A the axis about which M turns, and AR the reflected ray corresponding to an incident ray in the direction TA. M' is a plane parallel mirror mounted over the central scale division with the plane of its reflecting surface parallel to the line SS and capable of adjustment about that line as an axis but otherwise fixed with respect to the scale.

All adjustments, except the determination of the zero point, are made before the mirror M' is put in place and, after the scale has been placed as nearly as possible in the correct position by eye, the mirror M is turned so that the image of the central scale division falls on the intersection of the cross hairs. The mirror M' is then adjusted and the scale turned, about an axis parallel to A, until the mirror M intercepts the line of sight from the eye to its image in the mirror M'. When this condition is fulfilled the reflecting surface of M' is approximately normal to the line AR and the image of the axis A, due to successive reflections at M' and M, is visible in the field of view of the telescope if the focus is properly adjusted. Finally the image of A is brought into coincidence with the intersection of the cross hairs by cautiously continuing the adjustments of the scale and the mirror M'.

If these operations have been accurately performed the line of the scale is normal to the plane determined by the axis A and the line AR. Hence if M' is removed and the telescope focussed on the image of the scale in the mirror M the observed scale reading will be the true zero from which to reckon deflections. In general the point thus determined does not coincide exactly with the central scale division, unless that division lies on the axis about which the scale is turned in making the adjustments. For most purposes this is a matter of small moment, since it does not affect the accuracy of the measurements, made with the apparatus, and causes very little inconvenience in the reduction of the observations. It is obvious that any convenient scale division may be made to coincide approximately with the true zero point by placing the mirror M so that it reflects that division to the cross hairs of the telescope before the scale adjustment is commenced.

In practice the mirror M' is mounted on a stiff brass plate, about ten centimeters long and three centimeters wide, provided with three snugly fitting screws at right angles to its surface. The points of these screws are held firmly against the surface of the scale by a stiff spring and their position is fixed by a narrow slot and a small hole in a thin sheet of brass fastened to the scale so that the slot and the hole lie directly over the line of the graduations. The size of the openings is such that the screw points rest on the scale, but have no lateral freedom. The two screws resting in the slot and the hole are about ten centimeters apart and serve to adjust the mirror parallel to the line SS while the third screw turns it about that line as an axis. The mirror is placed as nearly as possible in the correct position by eye and the scale adjustment carried out as described above. The supporting plate is then turned through 180° in the plane of the scale and rotated about SS as an axis until the image of the axis A reappears in the field of the telescope. If this image does not coincide with the intersection of the cross hairs one half of the necessary correction is made with the screws that rest in the slot and the hole and one half by turning the scale about an axis parallel to A. The process is repeated until the coincidence is exact with the supporting plate in its initial and reversed positions. When this condition is fulfilled the plane of the reflecting surface of the mirror M' is parallel to the line of the graduations of the scale and that line is normal to the plane determined by the axis A and the line AR.

If the scale distance is one meter the virtual image of the axis A, due to successive reflections in M' and M, is situated approximately four meters from the telescope and it is easy to prove that the extreme scale divisions are equidistant from the axis A, within six tenths of a millimeter, when this image lies within one millimeter of the optic axis. This condition can be easily fulfilled with any good telescope, having sufficient aperture and magnifying power to allow readings accurate to one half millimeter on a scale at a distance of four meters, provided the mirrors are plane and the axis A or a parallel line within one millimeter of it is visible on opposite sides of the mirror M. With this method of adjustment as with any other the optic axis of the telescope must pass within one millimeter of

the axis A and remain within that limit throughout all the adjustments and the subsequent observations. All preliminary adjustments must, of course, be made with the necessary precision and the construction and disposition of the apparatus must be such that accurate observations are possible. For a discussion of these conditions the reader is referred to Holman's[1] admirable work.

[1] Holman, l. c.

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